the Acid Deposition Research Program

BIOPHYSICAL RESEARCH

EFFECTS OF ACID-FORMING EMISSIONS ON SOIL MICROORGANISMS AND MICROBIALLY-MEDIATED PROCESSES

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EXECUTIVE SUMMARY AND RECOMMENDATIONS FOR RESEARCH

Microorganisms are both directly and indirectly responsible for the welfare of higher plants. They directly affect mineral nutrition via symbiotic nitrogen fixation and mycorrhizal associations and adversely affect health by pathogenic attack. Indirectly, they are involved in the decomposition of organic matter and mineralization of plant nutrients.

Increases in hydrogen ion concentration as a result of acid deposition can affect the soil microflora directly by affecting cell membrane permeability and enzyme systems at the cell surface. The exposure of the cell surface to the anionic solubility products of SO_2 (i.e., sulphite and bisulphite) can also have direct toxic effects on microbial growth and reproduction although the importance of this relative to the hydrogen ion effect is not well understood. Indirect effects of acid deposition on microbial functioning include nutrient deficiencies caused by accelerated leaching of nutrient cations and phosphorus, solubilization of aluminum and iron to toxic levels, modification of plant physiological condition to a degree where root symbionts become less effective, and modification of the nutrient quality of plant residues available to the decomposer microflora.

In general, with the exception of the specialized S-oxidizing bacteria (*Thiobacillus thioxidans*), soil bacteria and actinomycetes tend to be inhibited by naturally acidic soil conditions below pH 5, whereas the fungi are less sensitive to soil acidification and may even flourish at low pH levels due to lack of competition from the bacteria. With the exception of sulphur oxidation, all microbially mediated processes proceed most readily at neutral or near neutral pH levels. Those processes which are mediated strictly by specialized bacteria (i.e., symbiotic N_2 fixation, nitrification) appear to be most sensitive to acidity, while ammonification and organic matter decay, which can be performed by the more acid-tolerant fungi at relatively high acidities, tend to be less sensitive.

At this point, it is difficult to determine if soil acidification caused by the deposition of acid forming emissions from anthropogenic sources has similar effects on the soil microflora and microbially mediated processes as natural soil acidification does. A comprehensive review of laboratory and field conducted studies has revealed that acidic inputs (primarily as simulated acid rain) can have widely varying effects on the various components of the soil microbial community. According to these studies, the soil pH levels at which significant alterations appear to occur are as follows: nitrogen-fixation (pH 6), nitrification (pH 6), ectomycorrhizae (not clear), vesicular-arbuscular mycorrhizae (pH 6), organic matter decomposition (pH 2-4), ammonification (pH 3), soil respiration (pH 3), carbon mineralization (pH 3), microbial community structure (pH 3-4), soil enzymes (not clear, but pH 2 simulated rain generally reduces activity). However, it should be kept in mind that the majority of studies dealing with acid deposition effects on soil respiration, carbon mineralization, microbial community structure, and decomposition/nutrient cycling processes have been conducted on naturally acidic forest

soils where an already acid-adapted microflora exists. Results from these studies, therefore, may not be directly applicable to less acidic grassland and agricultural systems where a more acid-sensitive microflora may predominate.

It should also be emphasized that in many controlled laboratory studies soil pH has been adjusted to extremely low values (i.e., <3.0), mainly in order to ensure a measureable negative impact on microbial processes within a limited period of time. It is doubtful that current legislation would allow the emission of pollutants to the degree necessary to reduce soil pH below 3.0 and, therefore, these laboratory studies may seem unrealistic. However, in special cases, such as S^{o}-dusted soils or soils found under S^{o} block base pads, the pH may drop well below 3.0 and in these situations the laboratory studies may be relevant.

Based on a review of close to 100 studies, the following general conclusions regarding the impact of acid forming emissions (mainly SO_2) on the microflora and microbially mediated processes can be made.

1. It appears that glucose mineralization patterns may be the best approach to identifying the effects of acid forming pollutants on the metabolic potential of the decomposer microflora. The relevance of pure substrate decay measurements to general decomposition and mineralization of plant residues in the field is uncertain. In Alberta, a reduction in glucose, cellulose, and vanillan decay as a result of acidification has been measured in the laboratory and this may be an indication of reduced organic matter decay in acidified soil in the field. However, this can only be substantiated by comparing decay rates of pure substrates and plant residues in the laboratory and the field.
2. Based on the results from both laboratory and field investigations, it appears that a reduction of naturally acidic forest soils to pH 3.0 or less will have an inhibitory effect on soil respiration. Due to the high buffering capacity of decaying plant residues and organic matter in the forest floor and the probable adaptation of an already acid-adapted microflora to further acidification, application of high dosages of SO_2 or extremely acid rain (i.e., pH 2.0) are necessary to reduce the soil pH to such an extent that microbial respiration is altered. Whether this is true of agricultural systems, where a more acid-sensitive microflora may predominate, remains to be determined.
3. Controlled laboratory and field studies have demonstrated that litter decomposition is retarded only if the plant residues are treated with extremely acidic (pH 2.0) rain or fumigated with high concentrations (530 ppb) of SO_2. Treatment with pH 3.0 to 3.5 rain has resulted in either no effects or an enhancement of litter decay. The litter acidities at which reductions in decay have been recorded are variable and include pH 1.8 and 3.7 to 4.1 for pine needles, pH 2.9 for spruce needles and

pH 3.7 to 5.0 for birch leaves. In the field, with uncontrolled inputs of acid forming pollutants, reductions in forest floor pH of 4.8 to 3.3 or 3.9 have resulted in increased forest floor organic mass due to a retardation of organic matter turnover.

4. The studies performed to date suggest that the activity of most soil enzymes is adversely affected by acidic deposition only if high dosages of extremely acid (pH 2.0) rain are applied to the soil. This is in agreement with soil respiration measurements which also appear to be sensitive to rainfall acidities below pH 3.0.
5. The majority of studies dealing with the impact of acid deposition on qualitative and quantitative aspects of the soil microbial community have dealt with chronic effects in the field and, therefore, the results may be applicable to some Alberta soils. It can be concluded that acidification of a naturally acidic forest soil (in Alberta, the pH of the surface soil in many coniferous forests ranges from 4.6 to 6.0) to approximately pH 3.0 or less results in a significant reduction in total microbial biomass. Bacteria are adversely affected at pH 4.0; fungi appear to be less sensitive to acidification but this may be an artifact resulting from methodological problems.
6. Certain factors in the N cycle are especially sensitive to acidity and thus could be adversely affected by acid emissions. There is little reduction in rates of ammonification until the pH reaches 3 or less but nitrification and N_2-fixation are inhibited in soils below pH 6. It is clear that the legume-*Rhizobium* symbiosis in Alberta is acid sensitive.
7. The effect of acid emissions on plant pathogenic relationships would appear to be very small under chronic regimes. Efforts would be best spent in evaluating leaf and stem diseases in unmanaged ecosystems.
8. Although studies in acid emissions and mycorrhizae are few in number, they indicate that these symbiotic relationships are largely resistant to chronic emissions. Most ectomycorrhizal plants are associated with a diverse array of acid-tolerant fungi which probably provides a strong buffering capacity against environmental changes. In possible contrast, at least some VA mycorrhizal fungi are acid-sensitive. Reductions of 0.5-1 pH unit may render certain VA mycorrhizal associations nonfunctional with a consequent reduction in plant growth.

RECOMMENDATIONS FOR RESEARCH

1. Research on soil and plant microbiology should be concentrated on unmanaged systems where acid emissions are most likely to have effects. Normal agricultural practices such as fertilization, liming, cultivation, pesticide applications, and harvesting will probably confound any subtle effects of wet or dry acid depositions and make their detection very difficult or impossible.
2. Emphasis should be placed on specialized organisms and processes that are directly related to plant nutrition. These include acid-sensitive prokaryotes which are responsible for symbiotic nitrogen fixation and nitrification and VA mycorrhizae.
3. Using well defined laboratory-greenhouse conditions, the effects of acidification on both ectomycorrhizal and VA mycorrhizal effectivity should be determined.
4. For biomonitoring purposes the effects of acid depositions on the decomposer organisms should be studied in terms of C-mineralization patterns from highly labile substrates such as glucose. This provides a rapid assessment of effects and appears to be a more sensitive indicator of change than the measurement of soil respiration.
5. More emphasis needs to be placed on the effects of soil acidification on microbial community structure particularly as it relates to changes in C(glucose)-mineralization patterns.
6. The relationship between acidification effects on glucose mineralization patterns and plant residue/organic matter decay rates should be addressed.
7. Additional research is required to understand the impact of acid forming emissions on nutrient mineralization from decaying organic matter. An attempt should be made to separate acidification effects on chemical release of nutrients from effects on release of nutrients due to mineralization activities of the microflora.
8. An integrated research program designed to understand the impact of acid forming pollutants on below-ground components should, firstly, determine the probability of alterations in soil pH based on pollutant deposition patterns and sensitivity of soil to acidification. If changes in soil pH have occurred or are imminent, then research should be directed to relating plant growth to acidification effects on nodulation/N_2-fixation potential (in the case of legumes), mycorrhizal (particularly VAM) relationships, glucose and nitrogen transformation potentials, plant residue and organic matter decay rates, and nutrient mineralization patterns. Microbial community structure should be determined in situations where a more detailed understanding of acidification effects on decomposition/nutrient cycling processes is required.

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1. INTRODUCTION

Soil systems are major receptors for anthropogenic acid forming emissions which are released into the atmosphere as byproducts of various industrial activities including fossil fuel combustion, oil and gas processing, pulp production and metallurgical processing. On a world wide basis, SO_2 and NOx comprise the largest component of acidic emissions, whereas on a more localized scale particulates such as atmospheric pollution deposits (soot) (Killham and Wainwright 1981) and S^o dust (Addison et al. 1984) may also form a large portion of the acidic inputs. Regardless of whether S-emissions are in gaseous or particulate form, they are ultimately converted to SO_4^{2-} salts and H_2SO_4 by chemical and/or biological means. Oxidation of SO_2 is predominantly a chemical process which may take place in clouds or fog droplets resulting in wet deposition of H_2SO_4 or in soil water following the adsorption or absorption of SO_2 by the soil (dry deposition). On the other hand, oxidation of S^o to SO_4^{2-} is mainly a microbial process mediated primarily by soil-dwelling Thiobacillus (chemoautotrophic bacteria) and some heterotrophic microorganisms (Wainwright 1984). Oxidation of SO_2 proceeds more rapidly than S^o oxidation.

The effect of acidity on soil chemical properties is comprehensively reviewed in Tabatabai (1985). The sensitivity of soils to acid forming emissions is dependent on the soil buffering capacity and its pH, with noncalcareous soils of low CEC and pH above 5 being more sensitive than very acid soils (McFee 1983). In a sensitive soil, excessive acid deposition may result in a reduction in CEC and base saturation with an increase in soil acidity causing enhanced leaching of aluminum, manganese, and nutrient cations (McFee 1983). The impact of acid deposition on soil physical and chemical properties may in turn have adverse repercussions on soil organisms and the decomposition and nutrient cycling processes which they mediate. The interactions of soil physical, chemical, and biological processes are ultimately expressed in a soil's fertility and its capacity for plant production. Consequently, much of the research conducted to date regarding the impact of acid forming pollutants on soil properties has been geared towards possible effects on plant productivity. This trend will be continued in this paper where the effects of acidic deposition on microbial communities will be reviewed in relation to potential impact on plant growth.

1.1 OBJECTIVES

The objectives of this review are to discuss:

1. The effects of acid forming emissions (primarily S-containing pollutants) on microbial community structure with emphasis on qualitative and quantitative aspects.
2. The effects of acidic deposition on microbially mediated processes (i.e., community functions). These include:
   a. carbon mineralization of pure substrates;
   b. nitrogen transformation processes such as asymbiotic N_2-fixation, ammonification, nitrification, and denitrification; and
   c. decomposition of plant residues.
3. Acidification effects of pollutants on symbiotic and disease-causing microorganisms. The symbionts to be discussed include ectomycorrhizal

fungi, vesicular-arbuscular mycorrhizal fungi, and N_2-fixing bacteria, particularly Rhizobium, while the disease-causing microorganisms will include those responsible for foliage, stem, and root diseases.

1.2 FUNCTIONS OF SOIL MICROORGANISMS

The soil microbial community is comprised of six main groups including the actinomycetes, algae, bacteria, fungi, protozoa and micro-invertebrates. The microbial biomass is dominated by the bacteria and fungi, forming approximately 25% and 75% of the total biomass, respectively (Anderson and Domsch 1978). It has also been estimated that 90% of the total respiratory metabolism in litter/soil systems is due to bacterial and fungal activity (Reichle 1977; Persson et al. 1980) with the remainder being attributable to the soil animals. For these reasons much of the research regarding acidic impacts on soil biology has concentrated on the bacteria and fungi and the functions they perform.

The roles of the soil microbial biomass in maintaining soil fertility have been summarized by Alexander (1980) and include:

1. The transformation of soil nitrogen, phosphorus, and sulphur from organic to inorganic forms making these nutrients available for utilization by plants.
2. The formation of humus which improves soil structure and promotes root growth due to better aeration and moisture conditions. Soil structure is also improved by the creation of soil aggregates which result from the binding properties of microbial excretions and fungal mycelial production.
3. The decomposition of organic matter and the detoxification of phytotoxins resulting from anaerobic decay processes.
4. The rapid degradation of toxic substances introduced into the soil including pesticides, herbicides, sewage sludge, and carbon monoxide. These activities are essential to the maintenance of environmental quality.

In addition, specialized bacteria and fungi which form symbiotic associations with the roots of many of the higher plants are vital in improving plant nutrition, resulting in enhanced productivity. Nitrogen-fixing bacteria (Rhizobium) form nodules on the roots of legumes and fix nitrogen from the atmosphere, making it available for plant growth. The plant in turn provides the bacterium with carbon. Ultimately, the decay of leguminous plant residues results in the accretion of soil nitrogen, thereby enhancing fertility. Mycorrhizal fungi are symbiotically associated with the roots of 95% of the higher plants. Due to their filamentous nature, these fungi are capable of exploring a larger volume of soil than roots alone for plant-essential nutrients such as phosphorus, a relatively immobile ion which is not as accessible to the plant as is nitrogen. The fungus absorbs the ion and transports it to the plant which in turn supplies carbon to the fungus. Numerous studies have demonstrated that under conditions where nutrients, particularly phosphorus, are limiting, mycorrhizal plants exhibit significantly greater shoot production and better phosphorus nutrition than non-mycorrhizal plants. There is also some evidence to suggest that the mycorrhizal relationship improves nitrogen nutrition, water relations, and disease resistance of the plant.

Clearly, both the N_2-fixing and mycorrhizal symbioses are fundamental to the maintenance of soil productivity.

In light of the fact that soil microbial processes are essential to the maintenance of soil structure, fertility, and plant growth, numerous investigations have been conducted to elucidate the impact of S pollutants on microbial structure and function, with subsequent speculation as to the eventual impact on plant productivity. Two main approaches have been taken in this research including:

1. Laboratory approach in which studies are performed under controlled conditions on intact soil cores or soil disturbed by mixing, drying, and remoistening. The experimental systems are usually plant-free and are treated with various dosages of acid forming substances including artificial acid rain (usually dilute H_2SO_4, HNO_3, or a combination), an acid forming gas (SO_2), or elemental S (sulphur dust). The bulk of the research appears to have taken this approach.
2. Field approach. In this case, the research can be categorized into two major groups: (a) those where defined areas of vegetation and soil (e.g., open top chambers, forest floor plots) receive controlled inputs of an acidic substance, usually dilute H_2SO_4, or a fumigant such as SO_2, and (b) those where the effects of an anthropogenic pollutant source (gas plants, coal-fueled power plants) on surrounding vegetation and soils are studied.

The effects of acidic substances or acid forming emissions on microorganisms in the soil or on the plant appear to be either: (a) acute, resulting from applications of high dosages of an acid over a short time span of usually days or weeks, or (b) chronic, resulting from the input of low dosages of an acidic material over the long term, usually years. In general, many laboratory studies have measured acute effects while field studies (particularly those conducted around a pollutant emitting source) have dealt with chronic effects. Whether acute effects bear any relation to chronic effects remains to be determined. Due to the variability in research approaches (i.e., diversity of soil types, pollutant dosages, exposure times) and the complex interactions of the soil microbes with the vegetation and soil chemical/physical characteristics, it may be difficult to generalize on the potential impact of acidic deposition on the soil microbial components.

1.3 INFLUENCE OF NATURAL SOIL ACIDITY ON MICROORGANISMS AND THEIR ACTIVITIES

Natural soil acidity is caused mainly by:

1. Reaction of atmospheric and soil-respiratory CO_2 with rainwater to form carbonic acid ($CO_2 + H_2O \rightarrow H^+ + HCO_3^-$);
2. Nitrification of ammonium ions ($NH_4^+ + 2O_2 + H_2O \rightarrow 2H_3O^+ + NO_3^-$);
3. Formation of organic acids from microbial decay of plant residues (McFee 1983); and
4. Plant production of CO_2, organic acids, and differential ion uptake.

A more detailed account of the mechanisms responsible for natural soil acidification is given in Tabatabai (1985).

The general effects of soil pH on microorganisms are presented in Tables 1 and 2 and can be summarized as follows:

1. With the exception of the specialized S-oxidizing bacteria (Thiobacillus thioxidans), soil bacteria and actinomycetes tend to be inhibited by acidic conditions below pH 5 (Table 1).
2. Fungi and protozoa exhibit no marked sensitivity to pH unless the pH is extremely low or extremely high. Fungi flourish at low pH levels due to lack of competition from the bacteria (Table 1).
3. Blue-green algae are sensitive to acidification below pH 5.0 while the Chlorophyta are less sensitive (Table 1).
4. With the exception of S-oxidation, all microbially mediated processes proceed most readily at neutral or near neutral pH levels. Those processes which are mediated strictly by specialized bacteria (i.e., symbiotic N_2-fixation, nitrification) appear to be most sensitive to acidity while ammonification and decomposition which can be performed by the more acid-tolerant fungi at relatively high acidities tend to be less sensitive.
5. Since a wide variety of microorganisms can oxidize inorganic S (e.g., heterotrophic fungi, bacteria, and actinomycetes in neutral or near neutral conditions and Thiobacillus thioxidans and possibly fungi in acidic conditions), S-oxidation appears to be relatively insensitive to soil pH.

1.4 GENERAL EFFECTS OF ACIDIC DEPOSITION ON SOIL MICROBES

Acidic deposition from anthropogenic sources may have both direct and indirect effects on soil microbes. Direct effects include:

1. Increasing the hydrogen ion concentration (pH) to levels where cell membrane permeability and enzyme systems located at the cell surface are altered. Also, at relatively low pH levels undissociated acids can enter the cells and damage them by changing internal cell pH.
2. The production of anionic solubility products which may or may not be toxic to microorganisms. For example, Babich and Stotzky (1978) tested a range of fungi and bacteria for their sensitivity to bisulphite (HSO_3^-) and sulphite (SO_3^{2-}) and observed that HSO_3^- was more toxic than SO_3^{2-}, particularly at a low pH (pH 6 and lower) where the main anion species was HSO_3^-. They argued that since all microbial cells are covered in a thin film of water the toxic effects of the highly soluble SO_2 could be due to the formation of HSO_3^- and SO_3^{2-} on the cell surface.

Indirect effects include:

1. An increase in leaching of nutrient cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) due to their replacement by H^+ on the exchange sites. The resultant nutrient deficiencies may alter microbial growth and reproduction.

Table 1. The effect of pH on soil microorganisms[1]

Organism	Effect
Actinomycetes	Low densities at pH<5.0; most abundant at pH 6.5-8.0. Not tolerant of low pH; Streptomyces exhibit poor growth and activity below pH 5.0; in highly acidic environments actinomycetes comprise <1% total viable count. Some acid-tolerant strains do exist.
Algae	Qualitative composition determined by acidity with each individual strain having an optimum pH and a range beyond which organism will not proliferate. Blue-green algae limited to neutral or alkaline conditions; absent below pH 5. Diatoms numerous in calcareous areas. Chlorophyta not as sensitive to pH and are present at wide diversity of pH levels - therefore Chlorophyta dominate algal flora in acid habitats.
Bacteria	Heterotrophic bacteria - optimum pH near neutrality; highly acidic conditions inhibitory. Greater the H^+ concentration, the smaller generally is the size of bacterial community. Soils at pH 3.0 still contain many bacteria. S-oxidizing bacteria - chemoautotrophs, particularly Thiobacillus thioxidans are capable of oxidizing elemental S to SO_4^{2-} and H_2SO_4. Thrive in acidic conditions with optimum growth between pH 2.0 - 3.5.
Fungi	Highly versatile; grow over wide pH range; in culture some have capacity to grow at pH 2.0 - 3.0. Fungi dominate habitats with low pH due to lack of competition from bacteria and actinomycetes for carbonaceous substrates. Individual species may demonstrate intolerance to high H^+ concentrations - may be important to plant pathogens e.g. Plasmodiophora brassicae performs best in acidic habitats while others grow best at neutral pH or higher.
Protozoa	No marked sensitivity to pH; some species in pure culture reproduce at pH 3.5. pH sensitivity is strain specific and some may not tolerate extreme acidity or alkalinity.

[1] Summarized from Alexander (1977).

Table 2. The effect of pH on soil microbial processes.[1]

Process	Effect
Ammonification	Ammonium and nitrate production from organic N is greater in neutral than acid environments. Acidification depresses but does not eliminate mineralization. Organic N accumulates in acidic soils. Ammonification carried out by fungi at low pH levels.
Decomposition	Usually proceeds more readily in neutral than acid soils. Many microbes capable of producing cellulases at neutral or alkaline pH; however, fungi responsible for cellulose degradation under acidic conditions. Cellulose decay rapid below pH 5.0 and sometimes below 4.0, but most rapid at higher pH levels. Composition of cellulose-decomposing organisms altered by pH; e.g., pH 6.5 - 7.0 - active population contains vibrios and fungi; pH 5.7 - 6.2 - fewer vibrios and more cytophagas; pH<5.5 - flora dominated by filamentous fungi. Fungi active in acidic soils, fungi and bacteria active at pH>6.0.
Denitrification	Many denitrifying bacteria sensitive to high H^+ concentrations. Acid soils tend to contain low numbers of denitrifiers. Some soils exhibit rapid denitrification at pH 4.7 so difficult to generalize on role of acidity in N volatilization. Acidity alters abundance of gases. N_2O produced below pH 6.0 - 6.5 and NO occurs at low pH levels. At neutral pH, N_2O reduced to N_2 so N_2 dominant above pH 6.0. Enzymes involved in N_2O reduction may be sensitive to acidity.
Nitrification	pH one of the major environmental variables affecting rate of ammonium oxidation. Difficult to assign exact limiting pH to the process since many physiological factors alter influence of pH. Nitrification usually falls below pH 6.0 and is negligible below pH 5.0. Acid-adapted bacterial strains may perform in soils of pH 4.5. Neutral to alkaline soils have greatest *Nitrobacter* populations. Acid-tolerant strains isolated from acid soils. Nitrification may be proportional to CEC.
Asymbiotic Nitrogen Fixation	Soils of pH<6.0 generally contain no N_2-fixing *Azotobacter* - also will not grow or fix N_2 in culture at pH<6.0. *Beijerinckia* more tolerant to acidity and will proliferate and fix N_2 from pH 3 - 9. Blue-green algae intolerant to acidities of pH 6.0 or less. Few N_2-fixing blue-green algae in acid forest soils. *Clostridium* acid tolerance between *Azotobacter* and *Beijerinckia*.
Symbiotic Nitrogen Fixation	Nodule formation in legumes of economic importance does not occur at pH<5.0. In pure culture *Rhizobium* growth sensitive to pH<5.0. Soybean is exception - nodules formed in highly acid environments. Toxicity may be result of Fe and Al in solution or Ca deficiency. Mb unavailable at high acidities and since this element is required in relatively large amounts for incorporation of N_2 into fixed forms, poor legume yields may result in soils of low pH.
Sulphur Oxidation	Not limited by pH. Production of sulphate from organic matter carried out by a wide range of microbes including many fungi, heterotrophic bacteria and chemoautotrophic bacteria such as *Thiobacillus novellus*. *Thiobacillus thioxidans*, a chemoautotrophic bacterium with a pH optimum between 2.0 and 3.5 is capable of converting elemental S to SO_4^{2-} and H_2SO_4 at a very rapid rate. Thus sulphur oxidation can proceed over a wide pH range, with the rate of oxidation being most rapid at low pH levels when *T. thioxidans* is active.

[1] Summarized from Alexander (1977).

2. Increase in solubility of aluminum and iron to levels where they become toxic to microorganisms.
3. A modification in the physiology of plants to a degree where root symbionts (N_2-fixers and mycorrhizal fungi) become less effective. The dry deposition and plant uptake of SO_2 may be an example of this. Also, changes in soil chemical/physical properties as mentioned previously may adversely influence plant growth with repercussions on the root symbionts.
4. A modification of the nutrient quality of plant residues available to the decomposer community. Uptake of SO_2 by the plant, dry deposition of SO_2 on plant surfaces and enhanced plant uptake of nutrients such as Al and Fe due to altered soil chemistry may change the chemical quality of plant residues which may indirectly influence the microorganisms.

Thus, it appears that the causes of any adverse effects of acidic deposition on soil microbes can be the result of a complex interaction of altered soil chemical/physical properties and altered plant growth and physiology. This makes it exceedingly difficult to understand precisely the factors which are responsible for any changes which may occur in microbial community structure and function as a result of acidification. It should also be kept in mind that acid-forming emissions such as NOx and SO_2 can enhance the nutrient status of nitrogen- and sulphur-deficient soils, resulting in positive effects on the soil microflora.

2. INTERACTIONS BETWEEN SULPHUR POLLUTANTS AND SOIL MICROORGANISMS: PURE CULTURE STUDIES

Although a comprehensive review (Babich and Stotzky 1982) of the effects of heavy metal pollutants on microorganisms is available, studies dealing specifically with the interrelationships between S pollutants and soil microorganisms grown in pure culture are summarized in Table 3. Generally the studies fall into two groups: (1) those which attempt to clarify the role of heterotrophic microorganisms in the oxidation of S^0, and (2) those which attempt to determine the concentration of SO_2 lethal to specific microbes or the effects of acidic substances on microbial growth rates and reproductive potentials. The majority of studies are based on the growth of specific microorganisms in synthetic media or sterilized soil amended or acidified with S^0, soot containing S, H_2SO_4, or salts of HSO_3^- or SO_3^{2-}. Investigations where microbes are exposed to SO_2 have also been performed.

The efficiency of the chemoautotrophic Thiobacillus sp. in oxidizing S^0 and acidifying their environment is well known (Vishniac and Santer 1957); however, the importance of the heterotrophic microbes, particularly the fungi, in oxidizing S^0 is less well understood (Wainwright 1984). Consequently, numerous studies have been conducted to determine the potential of heterotrophic bacteria and fungi to oxidize S^0 (Table 3). It has been established that some common soil fungi (Germida et al. 1985) such as Fusarium solani (Wainwright and Killham 1980; Killham and Wainwright 1981), heterotrophic bacteria (Pepper and Miller 1978; Germida et al. 1985) and actinomycetes (Yagi et al. 1971; Germida et al. 1985) are capable of oxidizing S^0 or S_2O_3 to S_4O_6 or SO_4^{2-}, both in synthetic media and sterilized soil. In the case of F. solani, S-oxidation increases with increasing pH (optimal pH = 7.0) with no oxidation occurring below pH 2.8 (Wainwright and Killham 1980). As well, increasing the C/N ratio of the media from 5:1 to 10:1 stimulates S-oxidation by this fungus. Pepper and Miller (1978) observed that, contrary to the autotrophic thiobacilli, the S-oxidizing heterotrophic bacteria required a carbon source to oxidize S^0 and that SO_4^{2-} accumulated in the media only when the bacteria entered the stationary phase. Based on in vitro S-oxidation by a range of bacteria and fungi, Germida et al. (1985) concluded that S-oxidizing heterotrophs formed two groups: (1) the rapid, complete oxidizers which were primarily the fungi; and (2) the slow, incomplete oxidizers dominated by bacteria and actinomycetes.

In addition to their S-oxidizing abilities, fungi (F. solani, Trichoderma harzianium) and bacteria (Arthrobacter globiformis) are also capable of concentrating S in their cells with increasing S supply by storing it as ester sulphates and amino acids (Saggar et al. 1981a). Of the hundreds of species of heterotrophic microorganisms inhabiting a typical forest or agricultural soil, only a very few have been tested for their S-oxidizing and immobilizing abilities. Generalizations about their importance in S-contaminated soils relative to the thiobacilli are therefore difficult to make. On the basis that fungi are more efficient at oxidizing S^0 to SO_4^{2-} and H_2SO_4 than are heterotrophic bacteria, it may be worthwhile comparing the S-oxidizing power of fungi which flourish in S-polluted soils to that of the autotrophic S-oxidizing thiobacilli inhabiting the same soil.

The inhibitory effects of a gaseous or heavy metal pollutant appear to be dependent on: (1) the concentration and chemical form of the pollutant; (2) the exposure

Table 3. S^o, SO_2 and S-compounds and soil microorganisms: effects on individual organisms tested in pure culture with emphasis on heterotrophic microbes.

Cultural Characteristics	pH	Test Organisms	Response	Reference
Pine needle fungi grown in synthetic media at different pH levels	3-6	Trichoderma harzianum Collybia acema Micromphalia perforans	-Tolerant of low pH -Tolerant of pH 3.0 -Not tolerant	1
Soil fungi grown on synthetic media and fumigated with SO_2	NR[1]	Alternaria, Penicillium Fusarium, Chaetomium Rhizoctonia, Trichoderma Aspergillus, Rhizopus, Colletrotrichum, yeast	-SO_2 uptake by all fungi N.B.: Ghiorse and Alexander (1976) postulated SO_2 may be adsorbed to microbial cells	2
S^o addition to synthetic media	NR	Fusarium solani, Trichoderma harzianum, Arthrobacter globiformis	-Increasing S supply increased S uptake, particularly by 2 fungi -Fungi store intracellular S as choline sulphate	3
Fungus grown in sterile soil and synthetic media amended with S^o	NR	Fusarium solani	-S oxidation increased with increasing pH; no oxidation below pH 2.8. Increasing C/N stimulated S oxidation. Spores germinate in presence of S^o	4
Synthetic media amended with atmospheric pollution deposits (APD)	NR	F. solani Thiobacillus thioparus	-Both released S-ions from APD. H_2S produced by F. solani. F. solani released S-ions from APD in sterile soil	5
Fumigation with 900-8500 ppm SO_2	NA[2]	Botrytis cinerea spores	-SO_2 toxicity dependent on concentration/exposure time. SO_2 more toxic as relative humidity (RH) increases due to formation of sulphurous acid	6
Fumigation with 50-8000 ppm SO_2	NA	Alternaria spores	-SO_2 toxicity to germination of Alternaria spores proportional to SO_2 concentration, exposure time, relative humidity. 100-400 ppm SO_2 reduced viability of wet spores; 500-4,000 ppm necessary at 90% RH. Spores may survive 10,000 ppm SO_2	7

continued...

Table 3 (Continued).

Cultural Characteristics	pH	Test Organisms	Response	Reference
Addition of S^o to sterile soil	NR	28 species of fungi from agricultural soil	-1 sp. Pencillium luteum oxidized $S^o \rightarrow SO_4^{2-}$	8
Addition of S^o or thiosulphate (S_2O_3) to synthetic media or sterile soil	NR	Two heterotrophic bacteria Thiobacillus thioxidans	-Heterotrophs oxidized S_2O_3 and S^o. SO_4^{2-} accumulates when bacteria enter stationary phase. Heterotrophs require C to oxidize S^o while Thiobacillus is inhibited by glucose. Heterotrophs probably primary S^o oxidizers in neutral and alkaline soils	9
Addition of various concentrations of salts of HSO_3^- and SO_3^- to synthetic media	7.0 6.0 5.0 4.0	5 spp fungi 4 spp bacteria	-Response species specific. HSO_3^- more inhibitory than SO_3^- to growth. Toxicity pH-dependent, the lower the pH the greater the toxicity	10
Synthetic media amended with 3.2 mM S as S^o, S_2O_3, or S_4O_6	NR	Thermophilic fungi Geosmithia argillacea Geosmithia emersonii Myceliophthora thermophila	-G. argillacea and G. emersonii oxidize S^o, S_2O_3 and S_4O_6 at 45°C and M. thermophila at 37°C. S^o, S_2O_3, S_4O_6 oxidized with intermediates at 25°C but not above	11
S^o added to synthetic media	NR	34 spp of Streptomyces (actinomycetes)	-31/34 spp oxidized $S^o \rightarrow S_2O_3$	12
Synthetic media amended with 1% flowable S	NR	11 bacteria 2 actinomycetes 3 fungi	-Fungi oxidized S to S_2O_3, S_4O_6 and SO_4^{2-}; bacteria exhibited incomplete oxidation of S to S_2O_3. Azospirillum and Rhizobium which are N_2-fixing bacteria oxidized S^o. Heterotrophic S-oxidation lower than S-oxidation by thiobacilli	13
Sterilized soil amended with 9% kaolinite or montmorillonite and acidified with dilute H_2SO_4	Untreated: 4.8-5.4 Treated: 3.2-3.9	4 fungi	-Reduction in soil pH to 3.5-3.7 resulted in reduction in growth with order of sensitivity being Penicillium brefeldianum>Aspergillus flavipes> A. niger>Trichoderma viride. Only T. viride grew at pH 3.2. Some slight amelioration of toxic effects by addition of montmorillonite	14

continued...

Table 3 (Concluded).

Cultural Characteristics	pH	Test Organisms	Response	Reference
Sterilized soil amended with clays adjusted to pH 3.4-4.6 with simulated acid rain consisting of a 2:1 solution of H_2SO_4:HNO_3	Untreated: 4.8-5.3 Treated: 3.4-4.6	Aspergillus	-No growth of Aspergillus at pH 3.5 -Toxicity mitigated by presence of kaolinite but not montmorillonite	15
Sterilized soil amended with Zn and Cd and acidified with 2:1 H_2SO_4 and fuming HNO_3	Untreated: 4.8 Treated: 3.4-4.2	Aspergillus niger	-Growth reduced at pH 3.6-3.9 and inhibited at pH 3.4. -Growth further inhibited by addition of Cd or Zn	16

[1] NR = not recorded
[2] NA = not analysed

References:

1. Abrahamsen et al. (1980)
2. Craker and Manning (1974)
3. Saggar et al. (1981a)
4. Wainwright and Killham (1980)
5. Killham and Wainwright (1981)
6. Couey and Uota (1961)
7. Couey (1965)
8. Abbott (1923)
9. Pepper and Miller (1978)
10. Babich and Stotzky (1978)
11. Wainwright (1984)
12. Yagi et al. (1971)
13. Germida et al. (1985)
14. Bewley and Stotzky (1983a)
15. Bewley and Stotzky (1983b)
16. Bewley and Stotzky (1983c)

time of the microorganism to the pollutant; (3) the physiological state of the microbes; (4) the morphological form of the microbe, for example, whether it is in a vegetative or resting stage; and (5) soil chemical, physical factors (Babich and Stotzky 1982). In terms of S pollutants, laboratory fumigation studies have shown that SO_2 toxicity to the germination of spores of two common fungal species is proportional to SO_2 concentration, exposure time, and relative humidity (Couey and Uota 1961; Couey 1965). Thus, 100-400 ppm SO_2 reduced the viability of wet spores, but 500-4000 ppm SO_2 was necessary to reduce germination when spores were held at 90% relative humidity. The high concentrations of SO_2 (1000-2500 ppm for 30 min) necessary to eliminate Alternaria spores on stored grapes suggests that fungal spores may be highly resistant to the toxic effects of SO_2, particularly when relative humidity is low.

It has been postulated that the toxic effects of SO_2 on microbial cells may be due in part to the anionic solubility products of SO_2, i.e., bisulphite (HSO_3^-) and sulphite (SO_3^-) (Babich and Stotzky 1978). After testing the toxicity of HSO_3^- and SO_3^- on five species of fungi and four species of bacteria it was observed that HSO_3^- was more toxic than SO_3^-, with toxicity increasing as pH decreased to 4.0. Considering that most microbial cells are covered with a thin film of water, it was concluded that SO_2, upon contact with the cell surface, could ionize to form highly toxic HSO_3^- especially at pH levels between 4.0 and 7.0.

The oxidation of gaseous and particulate S^o to H_2SO_4 results in an increase in H^+ and, depending upon soil CEC, a rapid or gradual reduction in pH. Fungi are generally accepted as being more tolerant to acidic (pH <5.0) conditions than bacteria; however, very few studies have been performed to determine the acid tolerance of various fungal species. Those which have been conducted suggest that tolerance is species specific with most fungi exhibiting reduced growth at pH 3.5-3.7 and very little growth below pH 3.0 (Abrahamsen et al. 1980; Bewley and Stotzky 1983 a,b,c). The presence of the clay, kaolinite, in the soil can mitigate the adverse effects of acidification caused by H_2SO_4, thereby lowering the lethal threshold for microbial growth and reproduction (Bewley and Stotzky 1983b). The effects of S-pollutants on organisms in various physiological conditions or morphological forms has received very little attention.

Unless the entire microbial community is investigated, the relevance of pollutant effects on organisms in pure culture to ecosystem function is questionable. However, in order to gain insight into the pollutant tolerance of what may be important "indicator" organisms or organisms which are potentially active in oxidation of S and soil acidification, it is necessary to conduct studies in vitro.

3. EFFECTS OF ACID DEPOSITION ON THE QUALITATIVE AND QUANTITATIVE ASPECTS OF THE MICROBIAL COMMUNITY

A major experimental approach to determining the effect of a pollutant on the soil microbial component involves the isolation of a specific component of the microflora by plating highly diluted soil slurries on synthetic media, counting the microbial colonies (assuming each colony has originated from an individual propagule), and isolating specific organisms in pure culture for subsequent identification. Criticisms of the dilution plating method include:

1. The use of synthetic media which selects for those organisms which are not specialized in their nutritional requirements (i.e., generalists). Consequently, a large proportion of the microbial community (depending on the soil) may not be evaluated using plating methods.
2. The selection for resting spores rather than the active vegetative cells. This applies particularly to the filamentous fungi where colonies isolated via dilution plating have been found to originate mainly from spores. In order to obtain a more realistic picture of the types of fungi active in a soil it is necessary to remove as many spores as possible (accomplished by soil washing) prior to plating litter or soil particles on synthetic media. More accurate estimates of fungal biomass can be obtained by microscopic examination of diluted soil and direct measurement of fungal mycelium.

Recently, indirect methods for determining total microbial biomass including the soil fumigation method (Jenkinson and Powlson 1976) and the physiological (glucose-stimulated respiration) method (Anderson and Domsch 1978) have gained popularity mainly due to their ease of use.

Due to the sheer number of microorganisms in a soil, particularly a highly organic soil, the analysis of the composition of a microbial community is a tedious and time consuming task. Consequently, very few investigations have dealt with this aspect in relation to S-pollutants. It could be argued that a knowledge of pollutant stress on microbial community structure and diversity gives little insight into pollutant effects on microbial community function and it is function not structure which is essential to the maintenance of a stable ecosystem. However, shifts in microbial diversity may be an indication of environmental stress (Atlas 1984) with species tolerant or physiologically adapted to a pollutant acting as "indicator" species. Just as response of the higher plant community to pollutant stress is often measured on the basis of plant diversity, so microbial diversity measurements should provide an indication of pollutant stress in the belowground system.

A summary of the effects of acid forming emissions on the qualitative and quantitative aspects of the microbial community is presented in Table 4. The majority of studies have been conducted in forest ecosystems many of which are naturally acidic and therefore, presumably, harbour an acid-adapted microflora. As mentioned previously, heterotrophic bacteria tend to be more sensitive to increasing soil acidity than the soil fungi and this is supported by the numerous investigations reporting significant reductions in heterotrophic bacterial numbers with the exposure or application of an

Table 4. Effects of acid-forming emissions on soil microorganisms: qualitative and quantitative effects

Pollutant and Source	Experimental System	Soil pH	Impact	Response	Reference
Simulated acid rain 0, 50, 100, 150 kg ha^{-1} H_2SO_4 applied annually for 6 y, Sweden	Field study humus layer in pine forest	Control 4.4 Acid 1:4.4 2:4.3 3:4.2	A→C[1]	-Active fungal biomass reduced in all treatments. Fungal numbers- no effect. Fungal community altered but few individual species affected. Oidiodendron sp increased in Acid 3 treatment	1
Simulated acid rain 0, 50, 150 kg ha^{-1} H_2SO_4 applied annually for 6 y, Sweden	Field-Pine forest A_{o1}-A_{o2},A_2, B horizons	Control 4.6-5.3 Acid 1: 4.2-4.9 Acid 3: 4.1-4.7	A→C	-Bacteria numbers, biomass, cell size decreased in A_{o1}-A_{o2}, active fungal biomass decreased in all horizons; fungal standing crop increased in A_{o1}, decreased in A_2, increased in B. Gram- bacteria dominant in control and spore-formers in acidified soil. Bacteria unable to grow at pH 3.5 and 4.0. Physiological capabilities of bacteria affected. Decrease in ammonifiers	2
SO_2 and S^o dust Gas plant, Whitecourt, Alberta	Field, pine forest, sandy soil; 3 sites located 3, 6, 10 km from point source	F/H: 3.4, 4.7 4.8. Mineral (0-10 cm): 3.8 5.7, 5.8	C	-Organic (F/H): total heterotrophic bacteria and starch utilizers reduced in site 1; spore formers not affected Fungal numbers unaffected, fungi in polluted site sulphite-tolerant, bacteria not sulphite-tolerant. -Mineral: total bacteria reduced in site 1	3
As in Ref 3	Pine needles, F/H; sites as for Ref 3	As for 3	C	-Needle and F/H fungi not different among sites. Aureobasidium dominant on needles; Trichoderma viride dominant in F/H	4
As in Ref 3	As in Ref 3 OM in F/H: 84-88%[2] OM in mineral: 2.6%	F/H: 2.8, 3.9, 4.3. Mineral: 4.1, 5.8, 5.6	C	-Microbial biomass reduced from 1560 to 890 mg C in F/H; no differences in mineral soil -Ratio of bacterial/fungal respiration in F/H was 5/95, 14/83, 18/82 and in mineral 31/71, 36/62, 38/62 at 3 sites, respectively	4

continued...

Table 4 (Continued).

Pollutant and Source	Experimental System	Soil pH	Impact	Response	Reference
Industrial emissions, Czechoslovakia	Field: Norway spruce F, H, A horizons	Control: 3.7-3.8 Acid: 3.6-3.9	C	-Bacterial numbers reduced (data variable, no significant effect) -Fungal numbers increased in F	5
As in Ref 5	As in Ref 5	As in Ref 5	C	-Same study as Ref 5. All data highly variable. Author concludes heterotrophic bacteria numbers, ammonifying bacteria reduced while fungal counts increase but no statistical tests applied. Mucor, Rhizopus increase while thiobacilli unaffected	6
As in Ref 5	As in Ref 5	As in Ref 5	C	-In polluted sites, proportion of pigmented bacteria increases, pseudomonads decrease. Site differences override effects of pollutants	7
As in Ref 5	Polluted to unpolluted transect from ash→dead spruce→live spruce F, H, A horizons	F: 3.0-4.4 H: 2.9-3.9 A: 2.9-3.8	C	-Aerobic bacterial numbers generally higher in ash regardless of pH (no variation presented)	8
As in Ref 5	As in Ref 5	As in Ref 5	C	-S-oxidizers increase with SO_4^{2-} content, but data variable. More thiobacilli in polluted soil. Addition of sulphite and sulphate salts reduces aerobic bacteria, ammonifying bacteria, thiobacilli, but not fungi	9
SO_2 emissions, industrial Czechoslovakia	Upper horizon of pine forest	NR[a]	C	-Bacteria, actinomycete counts increase, fungi decrease with distance from pollution source	10
Industrial pollution 50 y of SO_2 pollution. Unpolluted $45 \mu g SO_2 m^3 y^{-1}$ (120 ppb) Polluted: 90-125µg $SO_2 m^3 y^{-1}$ (240-334 ppb)	Sycamore woodland leaves, litter, soil	Litter: NR Soil (0-20 cm), Polluted: 4-4.2 Unpolluted: 6.0 pH lower under canopy	C	-S-oxidizing fungal counts: 17.8, 61.1, 195.0×10^2 in polluted leaves, litter and soil. 0, 0, 1.6×10^2 in unpolluted phylloplane, litter, soil	11

continued...

Table 4 (Continued).

Pollutant and Source	Experimental System	Soil pH	Impact	Response	Reference
As in Ref 11	Sycamore litter	NR	C	-Polluted leaves: 14-99x10²g⁻¹ thiobacilli, 6.3-31x10²g⁻¹ S-oxidizing fungi. Unpolluted leaves: no S-oxidizers. Polluted litter: 214-444x10² thiobacilli and 35-113 x 10² S° oxidizing fungi. More S°-oxidizing organisms below canopy than distant. Thiobacillus thioparus main autotroph on leaves; T. novellus in litter and soils. S°-oxidizing fungi: Alternaria tenuis, Aureobasidium pulluans, Cephalosphorium, Epicoccum nigrum, Penicillum	12
As in Ref 11	Sycamore woodland 4 cm below litter +10 cm; %C 5.8-7.2%		C	-Highest concentrations of S, S_2O_3 S_4O_6 and SO_4^{2-} below canopy in polluted area. Concentrations of S ions decrease with depth. S-oxidizing fungi and thiobacilli counts higher in polluted soils while heterotrophic bacteria are lower	13
As in Ref 11	As in Ref 11 Polluted/unpolluted soil exchange expt. CEC: 19mg 100g⁻¹	Unpolluted: 4.9 Polluted: 3.3	C	-Unpolluted soil pH dropped 1 unit after 12 mo in polluted site. Total heterotrophic bacteria decreased significantly in unpolluted soil after 12 mo exposure to pollution. Fungal counts unaltered. Numbers of thiobacilli and S-oxidizing fungi increased	14
As in Ref 11 Atmospheric pollution deposit (APD) or soot	Brown earth soil, sycamore leaves C=14.6%, N=0.9% S in APD=1.5%	3.6	C	-Fungi and yeasts observed in close contact with APD -Microbes oxidize and mineralize APD, releasing S ions into soil	15
Acid mine drainage Virginia	Field-aquatic system; leaves in creek	Control H_2O: 6.2-6.4 Acid 1: 5.4-6.3 Acid 2: 3.5-4.0		-No effect on bacterial standing crop but decay rates reduced	16
Simulated acid rain Soil from southern Alberta	Field soil Garden soil Acidified with H_2SO_4	Control: 6.8 Acidified: 2.9 Control garden: 7.7 Acidified: 3.2	A	-Heterotrophic bacteria reduced significantly after acidification of both soils	17

continued...

Table 4 (Continued).

Pollutant and Source	Experimental System	Soil pH	Impact	Response	Reference
S^o block near gas plant, Alberta	Soil adjacent and distant from S^o block	Control: 6.8 Acidic: 3.0	A→C	-Heterotrophic bacteria reduced significantly	17
Sulphur concrete cylinders buried in soil. Lethbridge, Alberta	Silt loam soil around cylinders analysed	Control: 7.0-8.1 Soil near concrete: no change after 3 growing seasons	C	-After 3 growing seasons, no reduction in heterotrophic bacteria in soil near cylinders. Less acidophilic T. thioparus detected in second growing season while more acidophilic T. thioxidans detected in third growing season	18
Unpolluted wheat, hay fields in Saskatchewan. S^o dusted forest soil downwind from S^o block. Strachan, Alberta	Soil plated on media containing .1-1.0% S for S-oxidizer counts Soil amended with 1% S to detect in vitro S oxidation	Wheat: 7.2-7.6 Hay: 5.5-5.7 Grass: 3.4 Forest litter: 1.3, soil 3.6	Field: C Forest: A→C	-No detectable thiobacilli in agricultural soils, but heterotrophic S-oxidizers present -Autotrophic thiobacilli in forest soil but no S-oxidizing heterotrophs -Main heterotrophic S-oxidizers were fungi	19
S^o dust downwind from S^o block Strachan, Alberta	Pine forest F/H, mineral (0-10 cm). 6 sites, 50-750 m from block OM=70-77% in F/H, 4-5.1 in mineral S increased from 2073µg g^{-1} to 19,000µg g^{-1} in F/H and 79-499 in mineral soil	F/H: 2.3-4.1 Mineral: 3.7-5	A→C	-Microbial biomass reduced from 930 to 160 mg $100g^{-1}$ with increasing acidity in F/H, no effect in mineral (28-33 mg $100g^{-1}$) -Highly significant relationship between pH and biomass in F/H	20
S^o addition to field soil Saskatchewan	Chernozem soil treated with S^o dust in laboratory	NR	A	-6.9-7.1 µg microbial biomass S g^{-1} soil (represents 2.3% of total S in soil)	21

[1] A = acute
C = chronic
[2]OM = organic matter
[3]NR = not recorded

continued...

Table 4 (Concluded).

References:

1. Baath et al. (1984)
2. Baath et al. (1980)
3. Bewley and Parkinson (1984)
4. Bewley (1986)
5. Langkramer and Lettl (1981)
6. Langkramer and Lettl (1982)
7. Lettl (1984)
8. Lettl (1985a)
9. Lettl (1985b)
10. Mrkva and Grunda (1969, quoted in Lettl (1984))
11. Wainwright (1978a)
12. Wainwright (1978b)
13. Wainwright (1979)
14. Killham and Wainwright (1984)
15. Killham and Wainwright (1981)
16. Carpenter et al. (1983)
17. Bryant et al. (1979)
18. Laishley et al. (1978)
19. Germida et al.(1985)
20. Visser (1984)
21. Saggar et al. (1981a)

acid forming substance to the soil. Although Baath et al. (1980) reported a reduction in bacterial numbers following acidification of a pine forest F/H horizon from pH 4.6 to 4.2, most investigators have observed a significant decrease in bacterial numbers only if the soil pH was reduced to less than 4.0 (Bryant et al. 1979; Wainwright 1979; Killham and Wainwright 1981; Langkramer and Lettl 1982; and Bewley and Parkinson 1984). The reduction in bacterial numbers following acidification is accompanied by an alteration in the composition and physiological capabilities of the bacterial community (Baath et al. 1980). Due to the resistance of the thick walled resting spore to acidification, spore-forming bacteria dominate the bacterial community following acidification (Baath et al. 1980; Bewley and Parkinson 1984) while the Gram negative bacteria are adversely affected (Baath et al. 1980). Reductions in ammonifying bacteria (Baath et al. 1980; Langkramer and Lettl 1982) and starch utilizers following acidification have also been reported. The decrease in bacterial numbers coupled with a reduction in cell size results in an overall decrease in bacterial biomass with progressive acidification (Baath et al. 1980). Additional support for this is provided by Bewley and Parkinson (1984) who measured the ratio of bacterial/fungal respiration and found that in the F/H horizon of a pine forest acidified with SO_2 and S° dust, this ratio decreased from 18/82 in the unaffected, pH 4.3 soil to 5/95 in the polluted, pH 2.8 soil.

In contrast to the heterotrophic bacteria, the activity of the chemoautotrophic, S-oxidizing thiobacilli (Thiobacillus thioparus, Thiobacillus thioxidans) is stimulated by the introduction to the soil of S-bearing substances such as atmospheric pollution deposits or soot emitted from industrial plants (Killham and Wainwright 1981), S concrete cylinders (Laishley et al. 1978), and S dust (Germida et al. 1985). The ability of the thiobacilli to utilize S as an energy source, thereby converting it to SO_4^{2-} and H_2SO_4, enables these organisms to flourish in S-enriched soils. The speed with which T. thioparus and T. thioxidans respond to the addition of S to soil appears to vary. Killham and Wainwright (1984), working in England, detected an increase in thiobacilli numbers after exposing an unpolluted soil to a pollutant source for only 12 months, while Laishley et al. (1978) detected the less acidophilic T. thioparus 12 months after burying S concrete cylinders in a neutral to alkaline silt loam in Alberta and the more acidophilic T. thioxidans 24 months after burying the cylinders. Elevated numbers of T. thioparus and T. thioxidans were measured in a dark brown soil in Saskatchewan which had received S° for 3 years prior to sampling and in the forest floor and mineral soil in a pine forest in Alberta which had been polluted with S° dust for a minimum of 3 years (Germida et al. 1985). The speed with which the thiobacilli respond and the rate at which S is oxidized upon the introduction of a S source is important since it will, depending upon the CEC of the soil, determine the rate of soil acidification. Interestingly, it is the acid production by the chemoautotrophic thiobacilli which has subsequent adverse repercussions on the heterotrophic bacteria.

Based on dilution plate counts, it appears that the heterotrophic soil fungi are little affected by acid deposition and soil acidification (Langkramer and Lettl 1982; Baath et al. 1984; and Bewley and Parkinson 1984) and may even thrive in these conditions due to a reduction in competition from the bacteria. The tolerance of the fungi to the potentially toxic HSO_3^- and SO_3^- ions (Bewley and Parkinson 1984) and the ability of some of the litter and soil fungi to oxidize S° to SO_4^{2-} (Wainwright 1978b; Wainwright 1979;

Killham and Wainwright 1984; and Germida et al. 1985) may contribute to the apparent insensitivity of fungi to S pollutants compared with the bacteria. One should keep in mind, however, that for the reasons mentioned previously, the dilution plating method is not necessarily the best method for determining pollutant effects on soil fungi. For example, dilution plate results suggest that acidification has little effect on soil fungi; however, Baath et al. (1980, 1984), using direct observation techniques, found that application of acid rain to a pine forest floor reduced fungal biomass while fungal standing crop increased - an increase which was attributed to a reduction in decomposition rates of dead mycelium. It appears, therefore, that the value of dilution plating for assessing pollutant effects on soil fungi may be questionable.

Studies dealing with the effects of acid deposition on fungal community structure are limited. Acidification of the F/H in a pine forest to pH 3.4 had no effect on fungal community composition (Bewley 1986), while application of 150 kg H_2SO_4 ha^{-1} annually for 6 years to the forest floor in a pine forest (thereby reducing soil pH from 4.4 to 4.2) altered fungal community structure with little effect on individual species (Baath et al. 1984). More critical research is required in this area before generalizations can be made.

Measurements of total microbial biomass (including both bacteria and fungi) may provide an overall indication of a microbial community going into stress as a result of S-pollution. The rapidity with which the microbial biomass can be measured using the Anderson and Domsch (1978) glucose stimulation technique makes this an ideal method for gaining a first impression of pollutant stress on soil microorganisms in general. In the F/H horizon of a pine forest contaminated with S^o dust, Visser (1984) measured a substantial reduction in microbial biomass with increasing soil acidity (pH 4.1-2.3). A highly significant (r^2 = 0.76) relationship existed between biomass and soil pH. Reductions in microbial biomass were particularly significant when soil pH fell below 3.0. Bewley (1986), using the same method, also measured a significant decrease in microbial biomass when soil pH was reduced from 4.3 to 2.8 in a pine forest acidified with SO_2 and S^o dust.

The majority of studies dealing with the impact of acid deposition on qualitative and quantitative aspects of the soil microbial community have dealt with chronic effects in the field and therefore, the results may be applicable to some Alberta soils. In summary, it can be concluded that:

1. Effects of S-pollutants in forest systems are usually restricted to the organic mat unless the mat is thin when the underlying mineral soil more susceptible to acidification. Also, S^o dusting may accelerate the acidification of the forest floor to such an extent that the mineral soil is also rapidly acidified.
2. Pollution of forest soils with S^o dust for a minimum of 3 years will result in rapid acidification due to the stimulation of S-oxidizing thiobacilli. In agricultural soils in Alberta, S-oxidizing thiobacilli require 2-3 years to manifest themselves after the introduction of a S source.

3. Acidification of a naturally acid forest soil to approximately pH 3.0 or less results in a significant reduction in total microbial biomass. Bacteria are adversely affected at pH<4.0; fungi appear to be less sensitive to acidification but this may be an artifact caused by methodological problems.
4. The impact of S pollutants on fungal community structure and the role of fungi in the oxidation of S^{o} dust is largely unknown and requires additional research.

Pollutant effects on microbial community structure provide little insight into the effects on microbial processes such as decomposition and nutrient cycling. However, coupled with other measurements such as glucose stimulated respiratory activity, substrate utilization rates, and decay rates of plant residues, the qualitative/quantitative aspects of the microbial community provide a more holistic picture and a better understanding of pollutant-microbial interactions. It should be emphasized that many of the results listed in Table 4 are part of more extensive studies where numerous microbial parameters were measured.

4. EFFECTS OF ACID DEPOSITION ON MICROBIALLY-MEDIATED PROCESSES

4.1 ACID DEPOSITION AND CARBON MINERALIZATION IN UNAMENDED SOILS

All heterotrophic soil microflora require carbon for energy, growth, and reproduction. Consequently, the decomposition of organic matter is considered the key microbial function in ecosystems, and for this reason it is the decay process which has received the most attention in acid deposition - soil microflora investigations.

One of the most common methods used to measure decomposition rates is the assessment of microbial activity via soil respiration. Microbial respiration is determined by measuring either O_2 uptake or CO_2 evolution by or from a specific area, volume, or weight of soil in the laboratory (where controlled conditions can be used) or in the field. The rate of microbial respiration is dependent to a large extent on soil organic matter quality (i.e., state of decay, C/N ratio, lignin content) and quantity, temperature, moisture, pH, and aeration. Variations in any of these factors will lead to variations in respiration measurements. Therefore, when monitoring a soil system (particularly over the long term) for the effects of an acid forming pollutant it is essential that the variation caused by such factors as temperature, moisture, and aeration be reduced as much as possible. This can be accomplished in the laboratory by determining respiration on soils which are held under optimum moisture, temperature, and aeration conditions for microbial activity. Soil organic matter quality can be standardized to a large extent by selecting organic material in various states of decay (e.g., brown leaves, grey leaves, fragmented leaves, amorphous organic matter) while the expression of results on an organic matter basis rather than total soil weight basis will reduce some of the variation caused by differences in soil organic matter content. Plant roots, which can be a major source of non-microbial respiration, can also be separated from laboratory processed soil samples. The lack of control of many of these factors in field conducted experiments versus the extent of control in laboratory conducted experiments may partially explain the inconsistencies often observed between the laboratory and field approaches.

The effects of acid forming substances on soil respiration have been followed in the laboratory and the field (in this case utilizing both controlled and uncontrolled acidic inputs). Of the 27 studies summarized in Table 5, 14 were conducted on laboratory processed soil samples, 7 on soils from field plots receiving controlled exposure to acid forming substances, and those remaining on soil samples from field plots in close proximity to pollutant sources. With the exception of one investigation (Bryant et al. 1979) all respiratory studies have dealt with naturally acidic ($pH<5.0$) forest soils. Acidic inputs applied to the various experimental systems (i.e., soil cores, soil column lysimeters, microcosms, individual soil or litter samples, field plots) have usually consisted of dilute H_2SO_4 (with or without the addition of base ions, HNO_3, or heavy metals), SO_2, or S^o dust. The wide variety of soil types, pollutant concentrations and pollutant loading rates (i.e., exposure frequency and time) utilized in many laboratory investigations has resulted in some contradictions among the results, making generalizations on the effect of acid rain difficult. For example, in a study conducted by Chang and Alexander (1984) the sheer number of treatments investigated, i.e., 3 sites, 2 soils/site, 2 depths/soil, and 3 acid rain concentrations applied at 5 different rates/soil, caused considerable confusion in the interpretation of the data.

Table 5. Acid deposition and microbial processes: effects on C mineralization in unamended soil.

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref.
Simulated acid rain 3:2 HNO_3-H_2SO_4 with base ions; rain adjusted to pH 2.0, 3.0, 4.0, 5.6	Forest soil-coarse, loamy, mixed mesic. CEC:19 mEq/100 g, OM-5.2%[1] Cores planted with 2 y old Ponderosa pine 15 cm rain applied over 12 wk 2 mm sieved soil	Control: 6.4 pH 4 rain: 6.3 3 rain: 6.2 2 rain: 3.5	A[2]	-Author concludes respiration stimulated using pH 3 and 4 rain. Data show no clear differences except with pH 2.0 rain which inhibited CO_2[3] -Author contends pH 4.0 rain increased C-availability but data do not support this. -NO_3-N, NH_4-N increased with pH 2.0 rain, no effect with 3.0 and 4.0 rain. Additional N inputs potentially stimulate respiration	1
Simulated acid rain identical to that for Ref 1	Same soil as Ref 1, sieved 1. pH 5.6 rain at .62 cm 2X/week for 26 wk 2. pH 3.0 rain at .62 cm 2X/week for 26 wk 3. pH 3.0 rain at 3.55 cm 3X/week for 3 wk 4. pH 2.0 rain at 1.06 cm 3X/week for 1 wk	Control: 6.4 1. 6.4 2. 5.8 3. 5.8 4. 5.3	A→C	-Soil pH changes restricted to top 1 cm -Microbial respiration stimulated by gradual H^+ input and inhibited by rapid H^+ loadings -Significant increase in available C with gradual input -Increase in NO_3-N and NH_4-N with rapid H^+ loading	2
Brick factory-SO_2 and soot emission. Unpolluted: 40 µg SO_2 m^3 (107 ppb) Polluted: 125 µg SO_2 m^3 (334 ppb)	Field study-brown earth in Sycamore woodland Soil exchange expt for 1 yr. Unpolluted soil in polluted site and vice versa	Unpolluted: 4.2 Polluted: 3.7	C	-Respiration, P-solubilization, and S-oxidation relatively unaffected by pH change -Ammonification increased, nitrification slightly decreased	3
Simulated acid rain. pH 3.5 4.1, 5.6 rain added daily for 14 d, at 12, 3-d intervals or 22, 7-d intervals. Rain composition based on ionic concentration of northeastern US rain	3 soils: 1) coarse, loamy coniferous 2) sandy, mixed coniferous 3) coarse, loamy deciduous. 3 mm sieved Cores-Organic + mineral layers %OM-Org: 17.1-49.3 Min: .5- 6.6 CEC: Org: 49-105 mEq 100 g^{-1} Min: 3-43 mEq 100 g^{-1}	1. Org: 3.6-4.1 Min: 4.1-4.6 2. Org: 3.1-4.5 Min: 3.9-4.8 3. Org: 3.8-3.9 Min: 3.8-4.1	A	-With few exceptions, leaching of C accelerated with more acidic rain -Organic matter decay (CO_2) reduced in samples where C-leaching reduced -Decay stimulated in samples where C was leached. Decay enhanced in some cases with acidic rain. Believed to be due to solubilization of organic matter by acid precipitation	4
Simulated acid rain. 8.4 cm applied 2X weekly. Rain pH=3.5 and 5.6. Soils received 58, 125, 208, 308 cm in 25, 53, 88 and and 130 d respectively	Soil coarse, loamy, mixed 4 mm sieved. Cores with mineral (2.3% OM) and organic (49.3% OM) layers	Org: 3.6 Min: 4.1 After rain: Org: 4.2 after pH 5.6 rain; 3.7 with 3.5 rain	A	-C mineralization reduced with pH 3.5 rain -Ammonium levels not altered by acidity -Nitrate formation inhibited with pH 3.5 rain	5

continued...

Table 5 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated acid rain. Pre-treatment: pH 5.7 rain for 3 mo. Treatment: 3.5 cm of pH 5.7, 4.0 and 3.5 rain weekly for 60 wk. H^+ ion deposition=36, 1840 and 5520 eq $ha^{-1}y^{-1}$	Undisturbed soil column lysimeters: 3 soils: 1) sand 2) sandy loam3) silt/ silt loam. Base saturation 1) 7-22%; 2) 3-14%; 3) 25-48%	Unpolluted: 1) 3.5-5.3 2) 3.1-4.6 3) 4.6-5.6 Polluted pH not presented	A→C	-CO_2↑ not affected by pH 3.5-5.7 rain -Edaphic factors override effects of acid precipitation -Leached DOC not significantly affected by pH 3.5 rain -C-turnover variable amongst forest types -DOC fractions altered by pH 3.5 rain i.e. 30-40% reduction in hydrophobic acid (Fulvic acid) content of leached DOC -DOC leaching patterns in field and lab correlated	6
Simulated acid rain Control: distilled H_2O Treated: H_2SO_4: 50 mmol m^{-2} (pH 3.0) 500 mmol m^{-2} HNO_3: 50 mmol m^{-2} 500 mmol m^{-2}	Field study: mixed deciduous woodland. Rain applied quarterly over 1 y. H^+ input 2-10X greater than normal US rain	pH: 4.6-5.0 in untreated soil Treated: NR	A→C	-No effect on CO_2↑, NH_4-N, NO_3-N, extractable P and Al -Slight but temporary increase in NO_3^- immediately after applying HNO_3^- -N-mineralization and nitrification unaltered -Seasonal effects significant and mask acid effects	7
Simulated acid rain; lake-water acidified to pH 3.0 and 3.7 with H_2SO_4/ HNO_3. Rainwater acidified to pH 3.7 with H_2SO_4/ HNO_3	Soil columns: 5 soil types with % C from to 38. Short term: .36 112 d with acidi-fied lakewater to 40 cm rain. Long-term: 690 d with acidified rainwater	Short term: 4.4-4.1; 3.9-3.5; 4.6-4.4 pH change in top cm of of soil. Long-term: no change in soil 1 (as in one) (4.1 -4.4); 3.9-3.5 and 4.6 -4.4 in other 2 soils	A→C	-Acid rain effects on CO_2↑ varied with soil type from no effect→stimulation→ inhibition in short-term experiment -Long-term: N_2 fixation and ATP unaltered. CO_2↑ dependent on soil type, either decreased or increased	8
Simulated acid rain Lakewater acidified to pH 3 and 3.7 with H_2SO_4/ HNO_3. Untreated: pH 4.6	Field plots: sandy soil. Total of 100 cm, pH 3.0 rain and 150 cm pH 3.7 rain over 180 d	Untreated: 4.5	A→C	-No effect on CO_2↑ -No effect on N-mineralization with pH 3.0 rain -Nitrification decreased with pH 3.7 and 3.0 rain (most sensitive parameter)	9
Simulated acid rain 1N H_2SO_4. Soil adjusted to pH 3.0 or 7.0	Sandy loam; pine forest air-dried and sieved (2.4 mm); 2.6-3.8% OM Decay of ground oak leaves added to soil	Adjusted to 3.2 (H_2SO_4) or 7.1 [$Ca(OH)_2$]. Natural acidic soil: 4.9	A	-Increase in CO_2↑ with increase in pH; artificial acidification reduced soil respiration by 52% and 37% in soil with leaf material -Ammonification reduced in pH 3.2 soil -Nitrate formation stimulated in pH 3.2 soil, but when amended with urea, little nitrate was formed -Denitrification reduced in pH 3.2 soil	10
Simulated acid rain. H_2SO_4/HNO_3 in 60:40 mEq H^+ ratio. Amended with metal ions and adjusted to pH 3.0, 4.0, 5.0	Fir/spruce needles mixed in 2:1 ratio	NR	A	-Litter sorbed more H^+ at pH 3.0 and 4.0 than 5.0 -K^+ leached most readily with acidified water -Wetting needles with pH 3 and 4 water reduced CO_2↑ -Pb and Zn in H_2O repressed CO_2↑	11

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Table 5 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated acid rain. Deionized H_2O, standard ionic composition, pH adjusted to 5.7, 4.5, 4.0 and 3.5 with H_2SO_4: HNO_3 (70:30 equivalent basis)	Microcosms; fine sandy loam, oak forest. Reconstructed soil profile allowed to settle for 6 mo planted with tulip poplar, oak, pine, litter replaced. CEC=2.0-3.1. Precipitation based on yearly average. Added over 30 mo period	Untreated: 5.3 Treated: NR	A→C	-No significant treatment effects on CO_2↑ -Environmental conditions important in controlling CO_2↑ -CO_2↑ from forest floor components (O1, O2 litter A_1 B mineral horizons, roots) showed significant stimulation of CO_2↑ only in O2 litter with pH 4.0 rain	12
Simulated acid rain. Dilute (0.8%) H_2SO_4 added as 0, 50, 100, 150 kg H_2SO_4 ha^{-1} and applied annually for 6 y	Pine forest; iron podzol A_{o1}/A_{o2}-humus	Control: 4.4	A→C	-CO_2↑ reduced in humus with all acid treatments	13, 14
As for Ref 13	Same as Ref 13 OM: 58-67%	Untreated 4.0-4.2 pH reduced up to 0.5 units	A→C	-CO_2↑ depressed by 150 kg acid treatment in one soil but no effect in another soil which contained more OM. Acid plus NPK fertilizer reduced CO_2 efflux even further	15
Simulated acid rain -same plots as in Ref 13 -used 150 kg H_2SO_4 treatment -acid treatment discontinued 3 y before sampling	-Same site and soil as Ref 13 -Used humus and mineral soil in microcosms; 90 d incubation	Control: 4.2-5.0 Treated: 3.8-4.5	A→C	-Reduction in C mineralization in acid treatment, stimulation when lime was added -Ammonium accumulation not depressed by acid -Turnover of N reduced by acidification	16
Simulated acid rain adjusted to pH 3, 2 with H_2SO_4. Control: Distilled H_2O (pH 5.6)	Spruce needle decay in lysimeters receiving 100 or 200 mm $month^{-1}$ twice weekly, 38 weeks	Control: 4.6-5.2 Treated: 4.2-5.1 with pH 3.0 rain; 2.9 with pH 2.0 rain	A	-Initially no consistent effects of acid rain on respiration; after 38 weeks pH 2.0 rain reduced CO_2↑	17
Simulated acid rain. 25 and 50 kg S $ha^{-1}y^{-1}$ as dilute H_2SO_4 (pH 3.1 and 2.7 rain). Applied at rate of 5 mm biweekly over 6 month period	Pine forest on podzol Mineral CEC:2.6-9.6 OM: .5-5.0% Lysimeter study	L: 3.9-4.0 F_1: 3.9-4.1 F_2: 3.6-4.2 H: 3.4-3.8 No effect of acid on pH	A	-Respiration in L, F_1, F_2 and H unaltered by acidic deposition. Fungal/bacterial respiration=90/10 - not altered by short-term acidification	18
Simulated acid rain. Fuming and non-fuming H_2SO_4, HNO_3, also HCl, H_3PO_3. All acids alone or in combination	Garden soil adjusted to 30 kPa tension with acidic water	Control: 5.0 Treated: 2.0-4.2 (immediate); 2.8-6.0	A	-At pH 2.3-2.4 fuming HNO_3 with or without H_2SO_4 inhibited CO_2 release	19

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Table 5 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated H_2SO_4 rain at pH 6.1, 4.0, 3.0 and 2.5. Applied once monthly during frost-free period at 50 mm per application	Spruce needles (L and H layers) collected after 27 waterings	Control: 4.2 Treated: 3.7-4.3	A→C	-Respiration not affected	20
SO_2 fumigation. 50 + 650 $\mu g\ m^{-3}$ (19 + 250 ppb)	Pine litter from 2 sites fumigated for 35 days	NR	A	-CO_2 efflux reduced. Respiratory contribution 80:20 fungi:bacteria	21
SO_2 fumigation 220 $\mu g\ m^{-3}$ (≈85 ppb)	Grass litter -finely ground	NR	A	-CO_2 efflux not affected	22
Sour gas plant SO_2 and S^o dust .19, .16 and .08 SO_2 equivalents 100 $cm^{-2}\ d^{-1}$ (2-10 ppb SO_2) Whitecourt, Alberta	Pine forest; 3 sites downwind Forest floor; L, F, H, mineral soil	F/H: 2.8, 3.9, 4.3 Mineral: 4.1, 5.8, 5.6	C	-Field CO_2↑ on organic mass basis always lower from forest floor at most polluted site -Laboratory: O_2↓ usually lowest for L, F, H, from most polluted site particularly from July to October -O_2↓ by decaying pine needles lowest in polluted site	23
As for Ref 23	Same site as Ref 23 F/H; mineral soil	As in Ref 23	C	-CO_2↑ from F/H lowest in polluted site -CO_2↑ from mineral soil unaltered	24
Oil production plant 6×10^5-1.2×10^6 tonne S over 24 y. Plant closed for 16 y prior to study. SO_2↑ currently <58 ppb. More heavy metals in contaminated plots	Sand, silt sediments Deciduous woodland 10 plots established downwind from closed plant Forest floor (0-3cm) Plots variable for vegetation, C/N, %C. Polluted:mor soil; unpolluted:mull	Polluted: 3.3-4.1 Control: 3.6-6.2 pH ($CaCl_2$)	C	-CO_2↑ and N-mineralization potential from polluted plots not significantly different from less polluted plots. Data variable due to lack of similarity among plots.	25
Simulated acid rain Diluted H_2SO_4	Field soil, garden soil; dried and sieved (2mm) and treated with dilute H_2SO_4 or distilled H_2O	Field: 6.8 Field treated: 2.9 Garden: 7.7 Garden treated: 3.2	A	-CO_2↑ in artificially acidified field soil, but not in artificially acidified garden soil	26
S^o block near gas plant, Alberta	Soil adjacent to block (1 mm) and distant (200 m) from block	Control: 6.8 Acidified: 3.0	C	-CO_2↑ significantly reduced in soil near S^o block	26

continued...

Table 5 (Concluded).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
S^o dust downwind from S^o block. Strachan, Alberta	Pine forest; 6 sites, 50-750 m from block; F/H, mineral (0-10 cm); OM: 70-77% in F/H; 4-5.1 in mineral; S increased from 2073 μg g^{-1} to 19000 μg g^{-1} in F/H and 79-499 in mineral soil	F/H: 2.3-4.1 Mineral: 3.7-5.0	A→C	-No significant effect of acidification on respiration (CO_2↑) of organic or mineral soil	27

[1] OM = organic matter
Org = organic
Min = mineral
[2] A = acute
C = chronic
[3] ↑ = efflux
↓ = uptake

References:

1. Killham et al. (1983)
2. Killham and Firestone (1982)
3. Wainwright (1980)
4. Chang and Alexander (1984)
5. Klein et al. (1984)
6. Cronan (1985)
7. Johnson and Todd (1984)
8. Bitton and Boylan (1984)
9. Bitton et al. (1985)
10. Francis (1982)
11. Moloney et al. (1983)
12. Kelly and Strickland (1984)
13. Baath et al. (1984)
14. Baath et al. (1979)
15. Popovic (1984)
16. Lohm et al. (1984)
17. Hovland et al. (1980)
18. Roberts et al. (1980)
19. Bewley and Stotzky (1983b)
20. Hovland (1981)
21. Ineson and Gray (1980)
22. Leetham et al. (1983)
23. Prescott and Parkinson (1985)
24. Bewley (1986)
25. Nohrstedt (1985)
26. Bryant et al. (1979)
27. Visser (1984)

As mentioned previously, one of the main factors affecting microbial activity is soil pH. Therefore, in order to simplify interpretation of the studies listed in Table 5, microbial response to acid forming substances will be discussed in relation to effects of rain or soil pH.

The majority of laboratory studies have dealt with effects of simulated acid rain, usually dilute H_2SO_4 or a combination of H_2SO_4 and HNO_3 adjusted to various acidities and applied to the surface of a soil column at different loading rates. The pH of the test soils usually has been <5.0 while that of the rain has ranged from 2.0 to 5.6 (control). Although individual rainfall events can range down to pH 3.0 (Likens et al. 1972) it has generally been accepted that simulated rainfall with a pH<4.0 represents a rainfall acidity considerably higher than that experienced by the microflora even under the most acidic rainfall conditions. In the laboratory, rainfall acidities of pH 3.0 or above have usually resulted in little or no effect on soil respiration (Killham et al. 1983; Johnson and Todd 1984; Kelly and Strickland 1984; Bitton and Boylan 1985; and Cronan 1985) unless the H^+ loading rate was high and rapid (Killham and Firestone 1982; Klein et al. 1984) or the simulated acid rain contained heavy metals such as Pb and Zn (Moloney et al. 1983). In some cases, particularly under conditions of gradual H^+ loading (Killham and Firestone 1982), rainfall acidities above pH 3.0 have been observed to stimulate respiration (Killham and Firestone 1982; Chang and Alexander 1984; and Bitton and Boylan 1985) and this has been attributed to a solubilization of organic matter (Killham et al. 1983; Chang and Alexander 1984). Sulphuric acid is commonly used for the hydrolysis of organic matter when analysing for lignin content (Allen et al. 1974); therefore, it is not surprising that simulated acid rain could cause some mild digestion of organic matter resulting in a release of microbially available C which could stimulate respiration if rainfall acidities are above the lethal threshold for most acid-adapted microorganisms. On the other hand, Cronan (1985) observed no effect of pH 3.5 rain on CO_2 efflux or leaching of total dissolved organic carbon (DOC) from three contrasting forest types although the fulvic acid content of the DOC was reduced with pH 3.5 rain. More attention should be directed toward elucidating the relationships between rainfall acidity, organic matter solubilization and microbial activity. Very few investigators have utilized simulated acid rain with a pH less than 3.0; however, those which have, have found that extremely acidic rainfall (i.e., pH 2.0) has a negative effect on soil or litter respiration (Hovland et al. 1980; Killham and Firestone 1982; and Killham et al. 1983).

Although the acidity of simulated acid rain is important in determining effects on microbial respiration, it is the soil pH which has the most direct impact on the microbial cell. Due to the importance of a soil's buffering capacity in controlling its pH, it is essential that in all simulated acid rain - microbial studies, both the pH of the rain and the soil are measured. As observed by Bitton and Boylan (1985) the impact of acid rain on various microbial parameters may vary with soil type. From those studies which have either adjusted soil pH with dilute H_2SO_4 or HNO_3, or measured soil pH after extensive treatment of the soil with simulated acid rain, it can be generalized that there is very little impact of soil acidity on microbial activity unless the soil pH is lowered below 3.5 and in most situations below 3.0 (Bryant et al. 1979; Hovland 1981; and Killham et al. 1983). The high buffering capacity of some soils and of decomposing

plant residues such as spruce needles necessitates the input of extremely acidic water (pH<3.0) in order to decrease soil or litter pH below 3.5 or 3.0 (Hovland et al. 1980). Also, the anionic constituents of simulated acid rain should be considered since HNO_3 has been observed to be more toxic than H_2SO_4 in soil respiration studies (Bewley and Stotzky 1983b). It appears that, based on simulated acid rain studies conducted in the laboratory, a rainfall acidity of pH<3.0 is necessary to adversely affect microbial respiration, while alteration of soil pH to 3.5 or less will usually inhibit CO_2 efflux.

Sulphur dioxide fumigation studies performed in the laboratory suggest that extremely high SO_2 dosages (250 ppb) are necessary before microbial respiration is reduced (Ineson and Gray 1980; Leetham et al. 1983).

A major criticism of laboratory studies is that the results are often difficult to extrapolate to the field situation. For this reason, various investigations have been performed in the field where naturally acidic forest floor plots are treated with controlled inputs of acid rain (Baath et al. 1979; Roberts et al. 1980; Hovland 1981; Johnson and Todd 1984;; and Bitton et al. 1981). Despite the fact that some of the studies failed to mention the pH of the simulated acid rain applied (Baath et al. 1979) or the effect of acid rain on soil pH (Johnson and Todd 1984; Bitton et al. 1985), it appears that a simulated acid rain pH of 2.5 to 4.0 applied over both the short term (Roberts et al. 1980) and long term (Hovland 1981) has negligible effects on soil respiration. With the exception of the study by Baath et al. (1979), simulated acid rain treatment did not reduce the soil pH below 3.5, possibly due to the high H^+ adsorption capacity of plant residues and organic matter in the forest floor. A soil pH of 3.5 or greater may be above the lethal threshold for many of the acid-adapted microflora characteristic of naturally acidic forest soils. If this is true, then the results obtained in the laboratory corroborate those obtained in controlled field experiments.

Ideally, the effects of acid deposition on microbial activity should be examined in field sites which are constantly exposed to uncontrolled emissions of acid forming pollutants. However, in investigations such as this it is often difficult to separate the effects of the acidic pollutant from the effects of edaphic factors such as topography and soil and plant community characteristics unless it can be established that both polluted and unpolluted sites were originally (i.e., prior to pollutant exposure) very similar. One method of overcoming the problems of site differences is to conduct a soil exchange experiment where intact undisturbed blocks of soil are removed from an unpolluted site and placed in a polluted site and vice versa (Wainwright 1980). However, in forest systems where removal of soil blocks would drastically disrupt the root systems of both overstory and understory plants this approach may not be feasible.

Another drawback of examining effects of environmental pollutants is that they often occur in combination, making it difficult to separate the impact of the individual pollutants. The majority of studies which have investigated the effects of uncontrolled inputs of acid forming emissions on microbial respiration have generally had to deal with emissions consisting of both SO_2 and particulate S° (Prescott and Parkinson 1985; Bewley 1986) or S-bearing soot (Wainwright 1980). With the exception of the study by Wainwright (1980), who measured very high concentrations of SO_2 (334 ppb) in close vicinity to the emission source, it is suspected that in the remaining studies (Bryant et al. 1979; Visser 1984; Prescott and Parkinson 1985; and Bewley 1986) much of the soil acidification

was a result of the oxidation of S° deposited on the soil surface during the dismantling of S° blocks created by the processing of sour gas. The levels of S° in soils in sulphur dusted sites adjacent to a sour gas processing plant (19,000 $\mu g\ g^{-1}$ in the F/H of the forest floor in a pine forest (Visser 1984) probably far exceed those resulting from wet and dry deposition of SO_2 (2-10 ppb).

Generally, the uncontrolled deposition of acid forming SO_2 and S° dust has resulted in a reduction in microbial respiration but only if the soil pH was lowered to 3.0 or less (Bryant et al. 1979; Prescott and Parkinson 1985; and Bewley 1986). However, Visser (1984) found that respiration of the forest floor in a S°-dusted pine site was little affected by acidification although soil pH ranged from 2.3 to 4.1. In this study, it was postulated that high inputs of plant residues (mosses, herbs, grasses, roots) killed as a result of S° dusting and acidification provided a highly labile food base, which, as evidenced by the greater CO_2 efflux per unit of microbial biomass in the polluted soils, was utilized less efficiently by the surviving, acid-tolerant microorganisms than was possible in the less polluted soils where labile C was presumably more limiting. This resulted in more CO_2 evolved per unit of C available in the polluted soils than in the less polluted soils.

Keeping in mind that the number of studies dealing with the impact of uncontrolled deposition of acid forming pollutants on microbial processes is limited, it can be concluded that, in Alberta (where the majority of studies have been conducted), reductions in soil respiration, particularly in forest soils, can be expected if soil pH is lowered to 3.0 or less. However, this pH threshold may be lowered in situations where high loadings of S° dust has caused severe mortality of the understory and large inputs of highly labile organic matter. Effects on microbial functioning from acidification of agricultural soils by acid forming pollutants have received very little attention in Alberta, possibly because the annual contribution of fertilizer to soil acidification (51 kg ha^{-1} $CaCO_3$ equivalents required annually for neutralization) far outweighs that from atmospheric deposition (2 kg ha^{-1} $CaCO_3$ equivalents required)(Sanderson 1984).

Based on the results from both laboratory and field investigations, it appears that a reduction of naturally acidic forest soils to pH 3.0 or less will have an inhibitory effect on soil respiration. Due to the high buffering capacity of decaying plant residues and organic matter in the forest floor and the probable adaptation of an already acid-adapted microflora to further acidification, application of high dosages of SO_2 or extremely acid rain (i.e., pH 2.0) are necessary to reduce the soil pH to such an extent that microbial respiration is altered. It should be kept in mind, however, that respiration measurements are not necessarily the most sensitive indicator of pollutant stress on the microbial community. Shifts in microbial community structure may take place with no obvious effects on soil respiration as a pollutant-insensitive component of the microflora replaces a sensitive one. However, on the basis of soil respiration determinations, the decay function of the soil microflora in forest soils is affected only when acidification stress is severe. Whether this is true in agricultural systems, where a more acid-sensitive microflora may predominate, remains to be determined.

Many investigators have stressed the importance of the decomposer microflora in nutrient cycling processes and the maintenance of primary productivity, and it has been automatically assumed that a reduction in soil respiration will lead to a depression in

primary productivity. Consequently, it is interesting to note that very few studies, particularly laboratory studies, have taken into account the interactions between the soil microflora and the plant. Whether or not a reduction in decomposer activity as a result of acidification stress actually leads to reduced primary productivity can only be determined if all three components of the ecosystem - plants, soil, and microflora are studied simultaneously.

4.2 ACID DEPOSITION AND CARBON MINERALIZATION IN SOIL AMENDED WITH PURE SUBSTRATES

In most soils, heterotrophic microbial activity is limited by a source of readily degradable carbon rather than by a supply of nitrogen, phosphorus, or other inorganic nutrients (Alexander 1977). For this reason, numerous investigators (Table 6) have studied the effects of acid forming pollutants on microbial respiration in soils amended with a readily utilizable C source such as glucose. Glucose is rapidly metabolized by the majority of soil microorganisms, thereby allowing them to express their full metabolic potential. When microbial cells are in a metabolically stimulated state the impact of an acidic pollutant would be expected to be more pronounced than when they are in the starved condition that is typical of most soils. This would suggest that glucose-stimulated respiration may be a more sensitive indicator of pollutant stress on the soil microflora than soil respiration alone.

Artificial acidification of soil with dilute H_2SO_4 or HNO_3 application of simulated acid rain and fumigation with SO_2 have had varying effects on glucose-stimulated respiration. Garden soil acidified to pH 2.8 or less exhibited a lag in glucose mineralization with complete inhibition occurring at pH 2.0 to 0.7 (Bewley and Stotzky 1983a). Nitric acid had a more toxic effect on glucose decay than H_2SO_4, while addition of 10,000 ppm Zn or 1000 ppm Cd to soil adjusted to pH 2.8 prolonged the lag in glucose degradation (Bewley and Stotzky 1983b,c). In contrast, artificial acidification of a field and garden soil (pH 6.8, 7.7) to pH 2.9 to 3.2 with dilute H_2SO_4 either stimulated or had no effect on glucose mineralization (Bryant et al. 1979). However, chronic acidification of the field soil (pH 6.8) to pH 3.0 as a result of S^o oxidation significantly reduced glucose decay (Bryant et al. 1979). Application of simulated acid (HCl) rain to three forest soils and one agricultural soil reduced soil pH to 3.7 to 5.6 and also reduced glucose mineralization but only in the upper 1.5 cm of soil (Strayer and Alexander 1981). These observations emphasize the importance of stratifying soil into various depths when searching for acidification effects on microbial activity.

Fumigation of a forest soil with high concentrations of SO_2 (1 ppm) reduced pH from 4.0 to 3.8 and inhibited mineralization of C^{14}-glucose (Grant et al. 1979a) with the degree of inhibition being dependent on length of exposure to SO_2. Bisulphite (HSO_3^-), the anionic solubility product of SO_2, inhibited glucose degradation particularly in acidified (pH 3.9) soil - an observation which supports that of Babich and Stotzky (1978), that reducing soil pH increases HSO_3^- toxicity. However, HSO_3^- is rapidly transformed to SO_2 (Grant et al. 1979a) so it is doubtful that HSO_3^- would have long-term effects unless the microbial cells were constantly exposed to it. Manganese and iron may also be solubilized in surface soil exposed to extremely high (10 ppm) concentrations of SO_2 (Grant et al. 1979b). Based on these studies, no clear patterns emerge regarding the effects of acid-forming pollutants on glucose metabolism by the microflora.

Table 6. Acidic deposition and microbial processes : effects on C mineralization in soil amended with pure substrates.

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated acid rain. Ionic composition of rain in NE US. pH adjusted with HCl to 3.2, 3.5, 3.8, 4.1 and 5.6 (control)	Silt loam; 3 forest soils; 1 agricultural; sieved, placed in core; 100 cm rain applied at 5 cm h^{-1} or intermittently 5 cm for 1 h, 3X/week; 7 weeks	Untreated: 6.6, 5.6, 4.4 and 7.1. Treated with pH 3.2 rain: 5.6, 4.7, 3.7 and 5.3 in in 0-1.25 cm deep soil	A[1]	-Acidic exposure with pH 3.2 rain significantly reduced pH in top 2 cm of soil, pH 4.1 rain had very little effect. Total acidity also increased in top 7.0 cm with pH 3.2 rain. pH 4.1-3.3 rain caused a steady decrease in pH and increase in Al, Ca, and Mg. Glucose mineralization reduced in top 1.5 cm of soil with pH 3.2 rain in all soils tested. pH 4.1 rain no effect on glucose mineralization. Intermittent acid rain at pH 3.2 also reduced glucose mineralization	1
Simulated acid rain. H_2SO_4 diluted in H_2O	Garden soil containing vermiculite, kaolinite, illite, mica and 5.8% OM[2] CEC = 8.2 mEq $100g^{-1}$. Soil stored for 8 y prior to use. This soil was amended with 9% kaolinite or montmorillonite. Soils brought to 30 kPa with acidified H_2O	Untreated: 5.0-5.4 Treated: 0.8-4.1	A	-Glucose mineralization not altered in pH 2.9 soil but reduced in soil acidified to pH 2.4. Addition of kaolinite and montmorillonite resulted in amelioration of acidic effects and reduced lag time prior to glucose mineralization. Amount of C mineralized was same in all soils irrespective of soil pH. Reduction of soil pH to 2.0-0.7 resulted in no CO_2 efflux unless inoculated with untreated soil	2
Simulated acid rain. HCl H_3PO_3; fuming and non-fuming H_2SO_4, HNO_3; alone or in combination (2:1 H_2SO_4, HNO_3)	Stored garden soil adjusted to 30 kPa tension with acidic water to give pH range of 2.0-5.0. Had to reinoculate soil due to lack of activity	Control: 5.0 Treated: 2.0-4.2 (immediate); 2.8-6.0 after 14 days incubation	A	-Acidification to pH 2.8 caused delay in glucose degradation with HNO_3 being most toxic followed by H_2SO_4. HCl and H_3PO_4 also reduced glucose decay. Amounts of C mineralized from soil treated with H_2SO_4/HNO_3 combined was intermediate between acids alone. No clear pattern of effects of acidity in uninoculated soil. Anionic constituents important.	3
Simulated acid rain. 2:1 H_2SO_4 and fuming HNO_3 Zn and Cd also added	Some soil as in Ref 2. Soil amended with glucose, Cd, and Zn and acidified	Untreated: 4.9 Treated: 2.8-4.7	A	-Adjusting soil to pH 3.2 and additions of 100 or 1000 ppm Cd or 1000 or 10,000 ppm Zn had no inhibitory effect on glucose mineralization. Soil adjusted to pH 2.8 caused lag in CO_2 efflux which was increased by addition 10,000 ppm Zn or 1000 ppm Cd	4
Simulated acid rain H_2SO_4 diluted in H_2O	Same soil as in Ref 2. Soil amended with 9% (kaolinite) or montmorillonite or left unamended. Vanillin added to soils	Untreated: 5.1 Treated: 1.8-3.8	A	-Very low $CO_2\uparrow$ from all treatments.[3] Soil required addition of active microflora before degradation commenced. Poor vanillin degradation in untreated and kaolinite-treated soil. Vanillin decay decreased with increasing acidification; complete inhibition occurring at pH 1.6. Postulates that glucose degradation less sensitive than vanillin degradation to acidification	5

continued...

Table 6 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated acid rain. Six annual applications of 150 kg H_2SO_4 ha^{-1}. Field experiment	Iron podzol dominated by pine forest. Soil samples taken 3 y after acid treatment was halted. A_o (humus) and A_1 (mineral) horizons were studied. %C=40.0 and 15%, respectively	Untreated: 4.2, 4.4 Treated: 3.8, 4.0	A→C	-Residual effects of acidification on glucose ^{14}C mineralization (23 and 15% lower in A_o and A_1). Over 90 d incubation higher proportion of labelled C was emitted as CO_2 from acid-treated soil than control. Acid treatment did not alter ammonium accumulation but reduced turnover rate of N	6
SO_2 and soot from coking works, England. 50 y SO_2 exposure. 150 µg m^{-3} (400 ppb) SO_2 to 200 µg m^{-3} (534 ppb) SO_2 emitted currently	Brown earth, some podzolization. Sycamore woodland. Cellulose amended soil packed in tubes and buried in polluted and unpolluted sites	Unpolluted: 4.9 Polluted: 3.3	C	-Cellulose decay slower in polluted soil but not markedly so	7
Simulated acid rain. 3:2 mixture of HNO_3:H_2SO_4 adjusted to pH 3.0, 4.0, 5.6. Ionic composition adjusted. Heavy metals added	Pine needles buried in litter bags in intact forest profiles in lab. Sprayed with acid rain	NR	A	-C^{14}-glucose stimulated respiration of pine needles not significantly altered by pH 3.0, 4.0, 5.6 rain. Also ratio of respired C to microbial biomass C not affected. Addition of low heavy metal load to pH 3.0 rain reduced respired C:biomass-incorporated C ratio, but not respired C alone. With high metal loading, pH 3.0 rain reduced both respired C and respired C:biomass C ratio.	8
Acid mine drainage due to pyrite mining (H_2SO_4 and heavy metals)	Field study-aquatic (creek and reservoir)	Control: 6.2-6.4 Acid 1: 5.4-6.3 Acid 2: 3.5-4.0	C	-Assimilation of C^{14}-glucose by heterotrophs in surface water was lowest in most acidic water. Glucose turnover 10X longer in most acidic environment	9
SO_2 fumigation. SO_2 diluted with air. Exposure 1µL SO_2L^{-1} (1000 ppb) 4 h-48 h	Forest soil, 16% OM sieved; exposed to SO_2 and HSO_3 and decay of C^{14}-glucose, C^{14}-protein, C^{14}-cellulose measured. Lab study	Untreated: 4.01 Treated 3.97-3.76	A	-Inhibition of C^{14}-glucose decay dependent on time of exposure to SO_2. Decay of C^{14}-protein hydrolysate reduced by exposure to 1 and 5 µL SO_2 but recovered rapidly when SO_2 removed. Cellulose decay little affected by SO_2. Bisulfite reduced decay of protein hydrolysate and glucose particularly in acidified soil pH (3.89). Majority (85%) of bisulfite formed from SO_2 was transformed to H_2SO_4 within 4 h. Unreacted SO_2 may be inhibitory to microbial activity	10

continued...

Table 6 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
SO_2 fumigation of soil with 1 ppm SO_2 for up to 72 h	Forest soil; 16% OM	Untreated: 4.06 Treated: 3.81-4.01	A	-C^{14}-glucose decay inhibited after SO_2 exposure for 48, 72 h. (pH: 3.95-3.84). 1 ppm NO_2 exposure for 13 d did not affect glucose decay. 5 µg bisulfite-S g^{-1} soil did not affect C^{14}-glucose decay but 5 µg nitrate-N did. A combination of nitrite and bisulfite had synergistic effect. Mn and Fe solubilized by high concentrations of SO_2 (10 ppm SO_2) but only in surface soil	11
Sour gas plant. SO_2 and S^o dust; .19, .16, and .08 SO_3^- equivalents 100 $cm^{-2}d^{-1}$ (2-10 ppb SO_2) Whitecourt, Alberta	Pine forest: 3 sites downwind from plant	F/H: 2.8, 3.9, 4.3 Mineral: 4.1, 5.8, 5.6	C	-Rate of glucose and vanillin decay in F/H measured as time required to attain maximum CO_2↑ after addition of glucose or vanillin was slowest in most acidic site. Total glucose-C mineralized not significantly different amongst sites, but more vanillin-C mineralized in most polluted soil. Glucose degradation not altered by acidification of mineral soil; decomposition of vanillin slowest in acidified mineral soil	12
Simulated acid rain Dilute H_2SO_4	Field or garden soil; dried and sieved (2 mm) and treated with dilute H_2SO_4 or distilled H_2O. Organic substrates then added	Field: 6.8 Field treated: 2.9 Garden: 7.7 Garden treated: 3.2	A	-Artificial acidification of field soil caused significant reductions in mineralization of starch and cellulose while mineralization of glucose was stimulated. Acidification of garden soil reduced decay of cellulose and casein but not starch and glucose	13
S^o dust from S^o block near gas plant, Alberta	Soil adjacent to block (1m) and distant (200m) from block	Control: 6.8 Acidified: 3.0	C	-Acidification due to oxidation of S^o dust caused significant reductions in mineralization of starch, cellulose, glucose, and casein	13
S^o dust downwind from S^o block, Strachan, Alberta	Pine forest; 6 sites, 50-750 m from block; F/H, mineral (0-10 cm); OM: 70-77% in F/H; 4-5.1 in mineral; S increased from 2073 µg g^{-1} to 19,000 µg g^{-1} in F/H and 79-499 in in mineral soil	F/H: 2.3-4.1 Mineral: 3.7-5.0	A→C	-Rates of glucose mineralization measured as time required to attain maximum CO_2↑ after addition of glucose exhibited a decreasing trend with increasing acidification in both mineral and organic soils. After 72 h incubation the amount of C mineralized from glucose-amended soils tended to be highest in organic soils below pH 3.0 and mineral soils below pH 4.5	14

[1] A = acute
C = chronic
[2] OM = organic matter
[3] ↑ = efflux

continued...

Table 6 (Concluded).

References:

1. Strayer and Alexander (1981)
2. Bewley and Stotzky (1983a)
3. Bewley and Stotzky (1983b)
4. Bewley and Stotzky (1983c)
5. Bewley and Stotzky (1984)
6. Lohm et al. (1984)
7. Killham and Wainwright (1981)
8. Killham (1985)
9. Carpenter et al. (1983)
10 Grant et al. (1979a)
11. Grant et al. (1979b)
12. Bewley (1986)
13. Bryant et al. (1979)
14 Visser (1984)

Using the method developed by Anderson and Domsch (1978), glucose-stimulated respiration can also be a measure of microbial biomass C. In this method, the quantity of glucose required to stimulate maximum respiratory activity is determined by applying a range of glucose levels to the test soils. The amount of glucose stimulated CO_2 released after the application of the optimum glucose level but immediately prior to the commencement of microbial growth can then be related to the microbial biomass C responding to the glucose addition using the regression equation: $y = 40.04x + 0.37$; where y = microbial biomass C (mg C 100 g^{-1} soil) and = x glucose stimulated CO_2 (mL 100 g^{-1} soil) released. By measuring microbial biomass C under standardized temperature, moisture, and aeration conditions it is possible to more accurately determine the impact of acidification on the soil microflora. Thus, Visser (1984) observed that in a pine forest acidified with S^o dust, respiratory activity was not altered in soils where the pH had been reduced to 3 or less; however, microbial biomass C was significantly reduced in organic soil below pH 3.3.

Possibly the most sensitive means of determining the impact of an acid-forming pollutant on microbial metabolic potential, which is probably governed to a large degree by the composition of the microbial community, is to study the kinetics of glucose decay after the addition of an optimum quantity of glucose. Lohm et al. (1984) observed that turnover of C^{14}-glucose was significantly reduced in a forest soil (pH 3.8, 4.0), 3 years after the application of 150 kg H_2SO_4 ha^{-1} y^{-1} was halted. In an aquatic environment, Carpenter et al. (1983) found that acidification to pH 3.5 to 4.0 caused by acid mine drainage reduced glucose turnover by a factor of 10.

In the F/H horizon of a pine forest acidified by SO_2 and S^o dust from a gas processing plant, the rate of glucose mineralization as measured by the time required to attain maximum CO_2 efflux after the addition of glucose was significantly slower in the most acidified soil (pH 2.8) compared with the less affected soils (pH 3.9 and 4.3), although the total glucose-C mineralized did not vary among the soils (Bewley 1986). Visser (1984) also measured a decreasing trend in time required to attain maximum CO_2 after glucose addition with increasing acidification of an organic soil polluted with S^o dust (38, 34, 26 19, 11 h in pH 2.3, 2.3, 2.6, 3.4 and 4.1 soils, respectively). Interestingly, in the mineral soils of the same sites, Visser (1984) observed no effects of acidification on either soil respiration or glucose-stimulated respiration; however, the time required to attain maximum CO_2 efflux after glucose addition was significantly longer in the most acidified sites (28 h versus 14 h in the least acidified soil). This suggests that alterations in the microbial community may be evident in the glucose metabolism patterns long before any changes in microbial respiration or biomass occur.

Variations in glucose turnover caused by a lag in glucose decay may indicate that specific components of the microflora in a pollutant-stressed soil are incapable of responding effectively to a highly available C source. The efficiency with which the microbial biomass metabolizes glucose may also be a sensitive indicator of acidification stress on the microbial community. For example, larger proportions of glucose C were evolved as CO_2 in acidified organic and mineral horizons in a pine site (Visser 1984). Lohm et al. (1984) observed a similar phenomenon in the humic and mineral horizons of a pine forest three years after acid treatment. In a study where pine needles were subjected to simulated acid rain (pH 3.0) amended with heavy metals, Killham (1985) measured

no effects on C^{14}-glucose stimulated respiration but found that the ratio between the C^{14} evolved as CO_2 and that incorporated in the biomass was significantly reduced by the acid/metal treatment. He suggested that this ratio would be a more sensitive indicator of pollutant stress on the microbial biomass than glucose stimulated respiration alone. Based on these studies it appears that glucose mineralization patterns coupled with glucose utilization efficiency may provide the most sensitive means of assessing pollutant stress on the microflora. Whether or not changes in microbial function as determined by glucose mineralization kinetics are related to shifts in microbial community structure is unknown.

In order to assess the impact of acid forming substances on the mineralization capabilities of specific components of the decomposer microflora, CO_2 evolution from soils amended with substrates less labile than glucose, such as cellulose, starch, casein, and vanillin, have also been investigated. Thus, Killham and Wainwright (1981) found that the decay of cellulose was reduced, but not markedly so, in acidified (pH 3.3) soils from sites which had been exposed to SO_2 and S-containing soot for 50 years. A significant decrease in the decay of cellulose, casein, and starch was also recorded in soils acidified from pH 6.8 to 3.0 with S^o dust (Bryant et al. 1979). However, fumigation of a forest soil with 1 ppm SO_2 for 4 to 48 h had little impact on cellulose degradation (Grant et al. 1979a). Due to the high degree of polymerization of the cellulose molecule, its rate of hydrolysis is slow and therefore the effect of acidification on cellulose decay should be followed over the long term (months, years) preferably using C^{14}-cellulose so evolution of CO_2 from the labelled cellulose can be separated from general soil respiration.

The mineralization of glucose is carried out by a wide range of heterotrophs including both acid-sensitive bacteria and the less sensitive fungi. Therefore, Bewley and Stotzky (1984) suggested that the activity of a specific component of the microflora such as the potentially more acid-sensitive aldehyde or vanillin degraders would be a more sensitive measure of the impact of acid deposition than would be the activity of the total heterotrophic population. However, the support for their argument is tenuous because the test soils which were artificially acidified and then amended with vanillin exhibited no vanillin degradation unless inoculated with an active garden soil. Consequently, the comparison of this study with those where no inoculation was performed (as in their glucose decay studies) is questionable.

Mineralization of vanillin was also determined in organic and mineral soils from a pine site acidified with SO_2 and S^o dust (Bewley 1986). In this study, the pattern of vanillin degradation in the organic soil as measured by time to attain peak CO_2 efflux after substrate addition was similar to that for glucose degradation - i.e., both glucose and vanillin degraded more slowly in the most acidified (pH 2.8) site. However, in the mineral soil glucose mineralization was unaffected by acidification, whereas vanillin degradation was reduced in the most acidified soil. This suggests that vanillin decay may indeed be more sensitive than glucose decay although in this case unamended respiration was just as sensitive to acidification as vanillin decomposition. Clearly, the use of vanillin degradation as a sensitive biomonitoring tool warrants further study.

In summary, it appears that glucose mineralization patterns may be the best approach to identifying the effects of acid forming pollutants on the metabolic potential

of the decomposer microflora. Vanillin decay patterns may be more sensitive but additional research is required before this can be stated unequivocally. The relevance of pure substrate decay measurements to general decomposition and mineralization of plant residues in the field is uncertain. In Alberta, a reduction in glucose, cellulose, and vanillin decay as a result of acidification has been measured in the laboratory (Bryant et al. 1979; Visser 1984; and Bewley 1986) and this may be an indication of reduced organic matter decay in acidified soil in the field. However, this can only be substantiated by comparing decay rates of pure substrates and plant residues in the laboratory and the field.

4.3 ACID DEPOSITION AND SOIL ENZYMES

The biochemical reactions involved in the degradation and mineralization of soil organic matter are catalyzed by proteins called enzymes. Although enzymes may be derived from soil animals, plant roots, and plant remains (Alexander 1977), their primary source appears to be the soil microflora. Microorganisms are unable to degrade such complex carbohydrates as cellulose, chitin, and pectin unless they produce enzymes which break down the complex substrates into forms which can be assimilated by the microbial cell. There are two groups of enzymes - those restricted to activities within the cell, the intracellular enzymes, and those active outside the boundaries of the cell, the extracellular enzymes (Alexander 1977). The relative contributions of intracellular and extracellular enzymes to total soil enzyme activity are difficult to separate (Tabatabai 1982), thereby causing problems in the interpretation of enzymatic activity measurements.

Soil enzyme reactions are assayed by incubating a soil sample with a substrate specific for a particular enzyme and measuring the rate of conversion of the substrate based on the amount of product produced or the amount of substrate lost over a particular period of time. Because soil enzyme assays are concerned primarily with extracellular or free enzymes, it is essential that the activity of the active microflora in converting the substrate or utilizing the products of substrate conversion be eliminated. This can only be accomplished by sterilizing the soil, which is a major problem since it must be done in such a way that intracellular enzymes are not released due to the rupture of viable cells and extracellular enzyme activity is not altered by the sterilant. In addition to the problem of soil sterilization, there are many factors which can have a bearing on the outcome of an enzyme assay, necessitating a thorough understanding of the reaction to be tested and the conditions required (e.g., temperature, pH, nutrients required to catalyze the reaction) to obtain peak performance by the enzyme. Extensive research on some of the enzyme-catalyzed reactions occurring in soil has allowed the standardization of assays for some of the enzymes active in the transformation of C, N, P, and S compounds. The procedures for the measurement of these enzymes, which include urease, phosphatases, arylsulphatases, rhodanese, dehydrogenases, and β-glucosidase, have been critically reviewed by Tabatabai (1982).

The soil enzymes which have been investigated with respect to effects of acid deposition include those important in S cycling (rhodanese, thiosulphate oxidase, and arylsulphatase), those which mediate N transformations (urease), those involved in P transformations (phosphatases), and those involved in the oxidation of C compounds

(dehydrogenases) (Table 7). Not surprisingly, the activity of rhodanese and arylsulphatase has been shown to increase with the chronic deposition of S-containing soot from industrial sources (Wainwright 1979; Killham and Wainwright 1981; and Lettl 1985a). Acute dosages of extremely acidic rainfall (simulated rain at pH 2.0) can, however, reduce arylsulphatase activity (Killham and Firestone 1982; Killham et al. 1983). The activity of urease, the enzyme which catalyzes the hydrolysis of urea to CO_2 and NH_3, appears to be unaffected unless the soil is inundated with high dosages of rainfall adjusted to acidities below pH 3.0 (Killham and Firestone 1982; Killham et al. 1983; and Bitton et al. 1985).

Similarly, the activity of phosphatases, the enzymes which catalyze the hydrolysis of both esters and anhydrides of H_3PO_4 (Tabatabai 1982), appears to be adversely affected by the application of simulated acid rain having a pH of less than 3.0 (Killham and Firestone 1982; Killham et al. 1983; and Bitton et al. 1985). The rate of H^+ loading may influence phosphatase activity although evidence for this is contradictory. Bitton and Boylan (1985) recorded a reduction of phosphatase activity with the application of simulated acid (pH 3.0) rain over the long-term (2 years), whereas Killham and Firestone (1982) observed an increase in phosphatase activity under conditions of gradual H^+ loading (pH 3.0 rain applied over 26 weeks).

Chronic treatment (2 years) of soil with pH 3.0 rain in the laboratory may also reduce the activity of the dehydrogenases, the enzymes which transfer hydrogen from substrate to acceptors during the oxidation of soil organic matter (Tabatabai 1982), although treatment of field plots with pH 3.0 rain had no effect on dehydrogenase activity (Bitton and Boylan 1985; Bitton et al. 1985). Also, reduction of soil pH from 4.2 to 3.7 had no adverse effects on dehydrogenase activity (Wainwright 1980). However, as has been noted for the enzymes discussed previously, treatment of soil with simulated acid rain of extreme acidity (pH 2.0) results in inhibition of dehydrogenase activity (Killham et al. 1983).

Proteases which are active in the conversion of proteins to amino acids tended to increase with the application of pH 3.0 rain and a subsequent reduction in soil pH from 4.5 to 3.3 (Bitton et al. 1985). Cellulases, the enzymes responsible for the hydrolysis of cellulose, were little affected by a reduction in soil pH from 4.2 to 3.7 (Wainwright 1980).

The pH stability of urease, acid phosphatase, alkaline phosphatase, and phosphodiesterase in three different soils adjusted to a range of pH levels with H_2SO_4 or NaOH has been investigated by Frankenberger and Johanson (1982). They concluded that reductions in enzyme activity at pH levels near the enzyme's optimum pH range were reversible, but that irreversible inactivation due to protein denaturation occurred when soil acidity or alkalinity became extreme. The acidities at which irreversible inactivation occurred varied with soil type. Both the source of the enzymes (i.e., plant, microbial, or faunal origin) and the adsorptive properties of the soil (high organic matter and clay content would protect the enzymes from pH denaturation) were believed to affect pH stability of the enzymes.

Studies designed to determine the effect of acid rain and soil acidification on enzyme activity (Table 7) have utilized a wide variety of soil types, which may explain the variability in results and the difficulty in drawing any definitive conclusions from

Table 7. Effects of acid deposition on soil microorganisms:enzymes.

Treatment	System and/or Soil	Soil pH	Impact	Response	Ref
SO_2-industrial pollution, Czechoslovakia	Spruce→dead spruce→ Mountain Ash F, H, A horizons	F: 3.0-4.4 H: 2.9-3.9 A: 2.9-3.8	C[1]	-Thiosulphate-cyanide sulfurtransferase (rhodanese), thiosulphate oxidase, and sulphite oxidase activity by bacterial isolates increased in dead spruce/ash soils	1
Industrial pollution >125 µg m^{-3} SO_2 (50 ppb); soot	Sycamore woodland; Upper 4 cm below litter →10 cm below; % C-5.8-7.2	Unpolluted: 5.8-7.6 Polluted: 3.9-4.7	C	-Rhodanese activity highest in polluted soils below canopy of Sycamore	2
Atmospheric pollution deposit (APD)	Brown earth soil; pH 3.6, 14.6%C, 0.9% N, Sycamore	pH 3.6-polluted	C	-Arylsulphatase activity increased in soil containing APD or sterile soil + APD + fungus (F. solani)	3
Simulated acid rain; 3:2 HNO_3-H_2SO_4 with base ions; adjusted to pH 2.0 3.0, 4.0, 5.6	Forest soil-coarse, loamy mixed, mesic. CEC 19 mEq/100 g; OM 5.2%;[2] cores planted with 2 y old Ponderosa pine; 15 cm rain twice weekly	Control: 6.4 pH 4 rain: 6.3 3 rain: 6.2 2 rain: 3.5	A	-Dehydrogenase increased slightly with pH 4 and 3.0 rain, reduced with pH 2.0 rain -With exception of urease which increased slightly with pH 4.0 rain, urease, phosphatase and arylsulphatase not significantly altered unless pH 2.0 rain applied. -Respiration less with pH 2.0 rain	4
Same as Ref 4 total rain added = 32 cm	Same soil as Ref 4 1. pH 5.6 rain at .62 cm 2X/week; 26 wks 2. pH 3.0 rain at .67 cm 2X/week; 26 wks 3. pH 3.0 rain at 3.55 cm 3X/week; 3 wks 4. pH 2.0 rain at 1.06 cm 3X/week; 1 wk	Control: 6.4 1. 6.4 2. 5.8 3. 5.8	A→C	-Soil pH changes restricted to upper 1 cm -Urease reduced with rapid H^+ loading (trt. 4) -Phosphatase increased with gradual H^+ loading (trt. 2) -Arylsulfatase increased with trt. 2 rain and reduced with trt. 3 and 4 rain -Respiration stimulated with gradual H^+ loading and inhibited with rapid H^+ loadings	5
Brick factory Industrial-SO_2 and soot emission Unpolluted:40 µg (107 ppb) SO_2 m^3 Polluted: 125 µg (334 ppb) SO_2 m^3	Field study-brown earth; Sycamore woodland soil; exchange expt. Unpolluted at polluted for 1 y	Unpolluted: 4.2 Polluted: 3.7	C	-Arylsulphatase, cellulase, dehydrogenase, phosphatase, rhodanese and urease and respiration not affected -Organisms adapt to acidic conditions	6

continued...

Table 7 (Concluded).

Treatment	System and/ System and/or Soil	Soil pH	Impact	Response	Ref
Simulated acid rain Lakewater acidified to pH 3.0 and 3.7 with H_2SO_4/ HNO_3; rainwater acidified to pH 3.7 with H_2SO_4/ HNO_3	Soil columns; 5 soil types with % C from .36 to .38 Short-term: 112 d with acidified lakewater to 40 cm rain. Long-term: 690 d with acidified rainwater	Short-term: 4.4→ 4.1; 3.9 → 3.5; 4.6 → 4.4. pH change in top cm of soil. Long-term: no change in 1 soil (4.1→4.4); 3.9→ 3.5 and 4.6→4.4 in other 2 soils	A→C	-No effect on dehydrogenase, phosphatase and protease in short-term expt. Respiration varied with soil type. -Long term: dehydrogenase and phosphatase reduced in 2/3 soils. Protease unaltered. Respiration dependent on soil type	7
Simulated acid rain. Acidified lakewater to pH 3.0 and 3.7 with H_2SO_4/ HNO_3. Untreated rain: pH 4.6	Field plots - sandy soil Total of 100 cm pH 3.0 rain and 150 cm pH 3.7 rain over 180 d	Untreated: 4.5	A→C	-Dehydrogenase, phosphatase, urease, respiration not affected by pH 3.0 rain. Protease increased slightly with pH 3.0 rain	8
Oil production plant 6×10^5-1.2×10^6 tonne S over 24 y. Plant closed for 16 y prior to study. SO_2↑ currently[3] <58 ppb. Heavy metals in contaminated plots	Sand, silt sediments; deciduous woodland; 10 plots downwind from closed plant; forest floor (0-3 cm); plots variable in vegetation, C/N, % C. Polluted: mor soil Unpolluted: mull soil	Polluted: 3.3-4.1 Control: 3.6-6.2 pH ($CaCl_2$)	C	-Phosphatase, dehydrogenase and respiration not significantly different in polluted and unpolluted plots; data highly variable	9
Simulated H_2SO_4 at pH 6.1, 4.0, 3.0 and 2.5. Applied once monthly during frost-free period at 50 mm per application in field	Spruce needles (L and F layers) collected after 27 waterings	Control: ≈4.2 Treated: 3.7-4.3	A→C	-Cellulase extracted from acidified samples tended to be less than that from control samples. Respiration unaltered	10

[1] A = acute
C = chronic
[2] OM = organic matter
[3] ↑ = efflux

References:

1. Lettl (1985a)
2. Wainwright (1979)
3. Killham and Wainwright (1981)
4. Killham et al. (1983)
5. Killham and Firestone (1982)
6. Wainwright (1980)
7. Bitton and Boylan (1984)
8. Bitton et al. (1985)
9. Nohrstedt (1985)
10. Hovland (1981)

the results. However, it does appear that unrealistically high dosages of extremely acidic (pH 2.0) rain will reduce soil enzyme activity, probably as a result of enzyme denaturation. Interestingly, this is in agreement with soil respiration measurements which also appear to be sensitive to rainfall acidities below pH 3.0 (see Section 4.1). Considering the ease with which soil respiration can be measured compared with the difficulties involved in the assaying and interpretation of soil enzyme activity, it could be argued that in an acid deposition biomonitoring program emphasis should be placed on measurements of soil respiration rather than soil enzymes. Rhodanese and arylsulphatase assays may be an exception since these enzymes could be indicative of S-transformation activity in those soils polluted with S-dust or S-bearing soot.

It has been stated previously that many soil enzymes are important in C, N, P and S cycling, and therefore may govern to some extent plant availability of key nutrients. Consequently, measurements of soil enzyme activity may provide an indirect means of determining the impact of acidic deposition on decomposition and nutrient cycling processes. However, a more direct and perhaps more accurate approach would be to determine the effect of acid-forming pollutants on rates of nutrient mineralization within the soil and decaying plant residues.

4.4 THE EFFECTS OF ACID DEPOSITION ON NITROGEN TRANSFORMATIONS IN SOILS

4.4.1. Introduction

A review of recent literature on the effects of acid deposition on nitrogen transformations in soils underscores the often variable and inconsistent nature of the results. This is not too surprising in view of the range of soil and climatic conditions encountered in the field, as well as the wide differences in experimental conditions employed in laboratory studies. Researchers have imposed either chronic acidity (i.e., dilute acid rain simulations for long periods) or acute acidity (i.e., concentrated acid rain simulations for short periods). Consequently, the interrelationships of time x acid dosage x soil type and how they affect microbiologically mediated processes involving organic matter and especially ammonification (i.e., N_2-mineralization), nitrification, N-immobilization, denitrification, and N-fixation are not well understood.

4.4.2 Organic Matter Decomposition and Ammonification

The decomposition of organic wastes and residues in soils by heterotrophic microorganisms generally results in the concomitant release of ammonia nitrogen into the soil environment. Once released, depending on the level of microbial activity and availability of carbon, the NH_4^+ can be: immediately immobilized back into the organic N pool; nitrified by autotrophic bacteria; or utilized by plants. Most of the researchers' results cited in Table 8 indicate that both organic matter decomposition (e.g., measured by microbial respiration) and ammonification are not greatly reduced by acid deposition until soil pH has reached a rather extreme value of about 3.0. This is especially true where soils are well buffered, have a reasonable level of organic matter and a high cation exchange capacity and high base saturation, all of which impart protection from acid deposition.

Table 8. Effects of acid deposition on nitrogen transformations in soils.

Treatment	Soil[1]	pH Initial/Final	Duration	Effects	Ref
Lab-Perfusion Study. Initial pH of the perfusate 6.0, lowered with H_2SO_4 to 3.0, 2.5 and 2.0. Acute	Sandy loam OM 5.8%[1]	4.8 initial, adjusted to 3.0, 2.5 & 2.0, (pH of perfusate)	50 days	-Ammonification not appreciably decreased, even at pH 2.0 ammonification of glycine reduced only 20%. Nitrification greatly decreased as the acidity of the perfusate increased	1
Soils taken from long-term field plots, treated and incubated in lab	Silt loam, OM 3.5%	4.8 initial soil pH. Field plots limed to pH 5.3, 6.0, 6.3, 6.6	15-35 days	-Ammonification not significantly different at any of the soil pH levels. The extent of nitrification in soil at pH 6.6 from addition of 100 ppm NH_4-N was 100% complete in 15 days. Corresponding values for pH values of 6.3, 6.0, 5.3, and 4.7 were 95, 80, 65, and 15%, respectively	2
Lab study	Sandy loam Agricultural soil having 20 year history of low pH	4.0 initial. Limed to 6.0	1 week	-Denitrifying activity higher at pH 6.0, but substantial denitrification detected in the acid soil. Conclude that acid-tolerant denitrifying population had been selected/adapted during the 20 year period	3
Lab study. Soils (3) collected and separated into organic and mineral layers, placed in pots in same order as found in field	Forest soils (3), (a) Organic (b) Mineral	(a) Initial 3.1-3.9-4.1 (b) Initial 3.9-4.1-4.6	Acid rain (simulated) at pH 3.5 or 5.6 for 2 to 12 weeks.	-N_2-fixation by algae in both the light and dark were less at pH 3.5 than 5.6	4
Lab study	Acid tea soils (kaolinitic)	Initial pH 4.0-4.5	2-6 weeks	-Substantial autotrophic nitrifying activity occurred in acid tea soils.	5
Chronic acid. Lab soil columns. pH of acid rain, 3.2-4.1	(a) Loamy sand; (b) Silt loam; (c) Silt loam	(a) 4.4-3.8 (b) 5.6-4.4 (c) 6.3-4.5	Continuous/ intermittent exposure, up to 19 weeks	-Increased N-mineralization, decreased nitrification due to acidity. Nitrate production inhibited in soil amended with NH_4^+, unaffected or stimulated in unamended soil	6
Lab studies. Acute acid treatment with 1N H_2SO_4 or liming	(a) Sandy loam; (b) Sandy loam	(a) 4.9-3.2; (b) 4.9-7.1	150 days	-N-mineralization decreased 50%. Nitrification and denitification decreased substantially due to acid treatment. Ammonification and nitrification increased when pH adjusted to 7.1	7

continued...

Table 8 (Continued).

Treatment	Soil	pH Initial/Final	Duration	Effects	Ref
Field study, site exposed to smoke plume from brick plant, SO_2 pollution chronic	Brown earth, soil taken from unpolluted site and exposed at polluted site	4.2-3.7	1 year	-No changes in microbial populations. No change in nitrification. Ammonification higher in the exposed, acidified soil than in transported soil	8
Lab study, acid rain pH 3.5 and 5.6	Three forest soils, coarse, sandy texture	3.4-3.9 initial pH	4, 14, or 24 weeks	-Mineralization less for soils exposed to acid rain at pH 3.5 than at 5.6. Inhibition of N mineralization decreased with increased exposure. Nitrification reduced by acid rain	9
Field plots, 150 kg H_2SO_4/ha/y Acute	(a) Forest soil; (b) Glacial till (c) Podzolized	(a) A_0 4.2-3.8 (b) A_1 4.4-4.0 (c) B 5.0-4.5	5 years	-Turnover rate of N in A_0 horizon reduced 50% by acid rain. Ammonification not significantly affected by soil acidification	10
Lab study. Simulated acid rain of 3:2 mixture of HNO_3:H_2SO_4. pH of 5.6, 4.0, 3.0 & 2.0. Acute	Forest soil, coarse sand gravel (mixed)	6.4 initial pH	12 weeks	-Accumulation of NH_4^+ and NO_3^- after rain of pH 2.0. Only acid rain at pH 2.0 caused significant inhibition of both respiration and enzyme activities. N-mineralization not adversely affected until rain of pH 2.0-3.0 was applied. Soil highly buffered. Change in soil pH occurred only after exposure to pH 2.0 acid rain (decrease from 6.4 to 3.7)	11
Lab study. Rain 4.0-4.1, adjusted to 3.5 and 5.6. Chronic	Forest soil (Spodosol) coarse-loamy texture	4.1 initial	45 days	-Both C mineralization and N mineralization progressively decreased with increased amounts of acid rain. Nitrification decreased as amount of acid rain increased	12
Field study. Acid rain up to 0.005 M Applied at rate of 70 kg acid per ha. Chronic/acute	Forest soil. (Typic Fragiudults) Frag. Pan at 50 cm depth	4.6-5.0 initial pH	11 months	-Rain using H_2SO_4 and HNO_3 at 2X and 10X the natural H^+ deposition had no effect on N-mineralization, CO_2 evolution, or nitrification	13

continued...

Table 8 (Concluded).

Treatment	Soil	pH Initial/Final	Duration	Effects	Ref
Lab study. Column leaching with acid rain at pH 3.5, 4.1 and 5.6	Forest soils - 0-15 cm organic layer and 20-35 cm mineral layer placed in columns in this order	Organic layer: 3.6-4.5 Mineral layer: 3.8-4.8	Up to 100 days	-Acid rain reduced amount of soil organic matter leached. As much as 1.0% of organic carbon leached during exposure period. In one soil, acid rain increased the leaching of organic matter. Acid rain reduced decomposition of organic matter in most cases, but stimulated decomposition in others. OM decomposition stimulated in soils where acid rain increased the amount of organic carbon leached. Decomposition inhibited where acid rain reduced organic C leached	14
Greenhouse plots spray irrigated with rain pH 2.0, 3.0, 4.0, and 5.6. Acute	(a) Sandy loam (b) Silt loam (c) Loam	(a) 6.4-7.4 (b) 5.3 (c) 5.3	10-12 weeks	-No effects of acid rain at pH 3.0, 4.0 and 5.6 on N_2 fixation, nitrification, denitification. Input of pH 2.0 decreased nitrification, increased denitrification, nitrate accumulation, pH decrease (soil) from 6.5 to 3.8, and stimulation of N-mineralization	15
Field plots, acid rain 100 kg H_2SO_4 per ha/y or powdered elemental S. Acute	Forest soil; glacial till, podzolized	A_0 4.2-3.6	3-4 years	-Addition of H_2SO_4 and elemental S inhibited CO_2 evolution. Acid rain stimulated N-mineralization	16
Field plots, H_2SO_4 150 kg/ha/y Acute	Forest soil, glacial till, podzolized		6-7 years	-Nitrification strongly reduced by soil acidification but markedly increased by liming. The extreme time x acid dose conditions resulted in an apparent increase in N-mineralization and accumulation of mineral N	17

[1] OM = organic matter

References:

1. Bewley and Stotzky (1983c)
2. Dancer et al. (1973)
3. Parkin et al. (1985)
4. Chang and Alexander (1983b)
5. Walker and Wickramasinghe (1979)
6. Strayer et al. (1981)
7. Francis (1982)
8. Wainwright (1980)
9. Novick et al. (1984)
10. Lohm et al. (1984)
11. Killham et al.(1983)
12. Klein et al. (1984)
13. Johnson and Todd (1984)
14. Chang and Alexander (1984)
15. Firestone et al. (1984)
16. Tamm et al. (1977)
17. Popovic (1984)

Tamm et al. (1977) reported that simulated acid rain (acute acidity) actually stimulated ammonification (i.e., N-mineralization) although organic matter decomposition (CO_2 evolution) was greatly retarded. They postulated that acid deposition inhibited N-immobilization because of decreased heterotrophic activity, and thus resulted in a net increase in N-mineralization. Other workers reporting an increase, or "stimulation", of N-mineralization from simulated acid rain also under conditions of acute acidity include Strayer et al. (1981), Firestone et al. (1984), and Popovic (1984). A biological explanation for a marked decrease in soil respiration/organic matter decomposition and a stimulation of N-mineralization may not be valid. Stimulation of this process was attributed merely to the accumulation of NH_4^+-N and there was no verification of whether a chemical or biological mechanism was involved. A more logical explanation, given the conditions of acute acidity, would appear to be the increased chemical extraction of organic matter and resulting acid hydrolysis which, in turn, released significant amounts of inorganic NH_4^+-N (Mortensen 1965; Stevenson 1965; Killham et al. 1983).

4.4.3 Extraction and Leaching of Soil Organic Matter by Simulated Acid Rain

Mineral acids such as HCl and H_2SO_4 have often been used to hydrolyze soil organic matter and extract such fractions as carbohydrates, and nitrogen and phosphorus compounds (Mortensen 1965). The fact that simulated acid rain, particularly with acute acidity, can hydrolyze and extract soil organic matter which can then undergo leaching to lower soil depths, seems to have been grossly overlooked by most researchers working on acid deposition. An exception was Chang and Alexander (1984) who reported that as much as 1.0% of the total organic carbon in some forest soils was hydrolyzed and leached during periods of simulated acid precipitation.

4.4.4 Effects of Acid Deposition and Simulated Acid Rain on the Nitrification Process

Nitrification is a two-step process that is classically performed by autotrophic bacteria in soils, i.e., Nitrosomonas sp. convert/oxidize ammonium to nitrite, and then Nitrobacter sp. further oxidize nitrite to nitrate. Obviously, these autotrophs derive energy from the process. A survey of the literature indicates rather conclusively that nitrification per se is a much more sensitive process than organic matter decomposition/ soil respiration or ammonification which are conducted by heterotrophic microorganisms having a wide range of physiological capabilities and tolerance to various sources of stress, including acid deposition.

Most workers have reported that nitrification is strongly and progressively inhibited with increasing levels of acidity. More often than not, soil pH is the parameter for correlating inhibition, and not total acidity. A general observation has been that when acid forest soils of pH 4.5 are further acidified by simulated acid rain to pH 3.5-4.0, there is a significant decrease in nitrification (Tamm et al. 1977; Strayer et al. 1981; Francis 1982; Bewley and Stotzky 1983c; Klein et al. 1984; and Novick et al. 1984). Acute acidification of soils to a pH range of 2.0-3.0 leads to a total suppression of the nitrification process (Bewley and Stotzky 1983c; Killham et al. 1983; and Firestone et al. 1984).

In cases of chronic acidity where carbon mineralization is inhibited, the nitrification process is also markedly suppressed and there is little or no accumulation

of NH_4^+-N, nor is there any evidence of stimulated N-mineralization that has been reported by some workers who have imposed acute acidification treatments on forest soils (Klein et al. 1984).

Walker and Wickramasinghe (1979) studied the presence and activity of Nitrosomonas sp. in acid tea soils of Sri Lanka and Bangladesh and reported substantial autotrophic activity of this genus in the range of pH 4.0-4.5. However, these soils were not exposed to acid rain and had undergone long-term natural acidification wherein these organisms had adapted/adjusted to such conditions. On the other hand, Dancer et al. (1973) reported that a soil which had reached pH 4.8 from natural acidification over a long term had a rather low nitrification potential compared with the same soil when limed. They speculated that this was probably due to a diminished population of Nitrosomonas sp. as the soil became progressively acidified.

Strayer et al. (1981) presented some data which suggests that NH_4^+ was nitrified by heterotrophic microorganisms in soil exposed to acid rain. This possibility is based on their work with Nitrapyrin or N-Serve, a nitrification inhibitor [2-chloro-6-(trichloromethyl) pyridine] which specifically inhibits the genus Nitrosomonas that oxidizes NH_4^+ to NO_2^- (Parr 1973). Despite the use of this compound, only partial inhibition of nitrification was obtained. Thus, nitrification in their acid rain treated soil may have been a function of both autotrophic and heterotrophic microorganisms.

4.4.5 Time X Acid Dosage Relationships

Wainwright (1980) reasoned that many soil microorganisms, both autotrophs and heterotrophs, are probably capable of adapting to acid stress and acidification, provided that acid inputs are reasonably small and occur over a sufficiently long period of time. Chronic acidity would allow many soil microorganisms to adjust to progressive acidification through either simple adaptation or even mutation. On the other hand, acute acidity would not afford such adjustments and could totally eliminate certain beneficial types of organisms from the ecosystem. Moreover, it may then be virtually impossible to re-introduce these "lost" species by means of inoculation.

Such concern for the time x acid dosage relationships in soil from acid deposition was also expressed by Novick et al. (1984). They criticized the single dose-acute acidity approach as totally unacceptable to the study of long-term exposure of soils and their chemical/biological processes to acid deposition. They also argued that under natural conditions, soil microorganisms can and do have time to acclimate to changes in their environment, whether the stress factor stems from acidity, alkalinity, moisture, or temperature. Thus, sensitive populations over a period of time could be replaced by species that are more resistant to the stress. It follows then that the results of short-term studies involving acute acidity may be grossly misleading because under long-term/chronic acidity conditions soil microorganisms may indeed adjust/adapt to acid stress and new resistant populations may become established (van Loon 1984).

4.4.6 Effects of Soil Acidification and Simulated Acid Rain on Denitrification and Nitrogen Fixation

In a study which did not involve acid deposition or acid rain, Parkin et al. (1985) characterized the denitrifying activity in a soil that had a 20-year history of

natural soil acidification (including the effects of acidification from chemical fertilizers) and had reached pH 4.0. Samples of this soil were also limed to pH 6.0 for comparative purposes. Substantial denitrifying activity was detected in the acid soil, i.e., approximately one-third of the denitrification rate that was measured for the limed soil. These authors concluded that acid tolerant denitrifying microbial populations had been selected/adapted during the 20-year period of low soil pH.

A study by Firestone et al. (1984) involving acute acidity where simulated acid rain (pH 2.0) reduced the pH of a soil from 6.5 to 3.8, resulted in markedly decreased nitrification, increased nitrate accumulation, and increased denitrification. These workers reasoned that the increased denitrifying activity was associated with the increased availability of dissolved organic carbon from acid hydrolysis and extraction of soil organic matter. These results are of questionable validity in view of the extremely acidic inputs that were employed.
The most useful conclusion here is the one reached by the authors, i.e., that "short-term acute effects should not be used to predict long-term chronic effects of acid rain on soil microbiological processes."

In cases of long-term chronic acidity, it is possible that substantial losses of nitrogen could occur from soils as carbon is solubilized from acid hydrolysis of organic matter and leached downward in the profile with NO_3^-. Then, with intermittent periods of soil anaerobiosis (e.g., from heavy rains) the stage would be set for rapid denitrification.

Chang and Alexander (1983b) studied the effect of simulated acid rain at pH 3.5 and 5.6 on the rate of N_2-fixation by indigenous soil algae. They found this particular N_2-fixation pathway to be highly sensitive and noted a significant decrease in N_2-fixation with increasing acidity. They concluded that algae in terrestrial ecosystems will be especially susceptible to acid rain because their proliferation occurs mainly at the soil surface where acid stress is initially greatest.

There has not been very much research done on the effects of acid deposition or acid rain on either denitrification or free-living N_2-fixation. Certainly, denitrification, which can be performed by a wide range of facultative anaerobic microorganisms, which are heterotrophic, is a less sensitive process than N_2-fixation as performed by algae, Azotobacter or the symbiotic Rhizobium. The effect of acid deposition/acid rain on all of these N_2-fixation pathways should be investigated.

4.4.7 Summary and Conclusions

McFee (1983) attempted to put acid deposition in proper perspective by differentiating between it and soil acidification. The latter process is usually of considerably greater magnitude and includes acid inputs to soils from nitrification, organic matter decomposition, root respiration, respiration by soil microorganisms and CO_2 production therefrom, as well as acidifying effects from N-P-S chemical fertilizers. Acid deposition as SOx and NOx emissions from industrial and atmospheric sources which might contribute to soil acidification are usually 1 to 2 orders of magnitude smaller than the combined sources listed for soil acidification. Nevertheless, there are indeed cases and locations where the magnitude of acid deposition is much higher. Moreover, there are many inconsistencies and rather conflicting results on the effects of acid

deposition and simulated acid rain on various chemical and biological processes in soils, mainly because of the interactions of time x acid concentration x total acidity x soil type, as well as other widely different experimental conditions. In view of this, there is a need to clarify the effects of both chronic and acute acidity on nitrogen transformations in soils affected by acid deposition.

4.5 ACID DEPOSITION AND DECOMPOSITION/MINERALIZATION PROCESSES

Ecosystems are comprised of three main functional units, the plants, the herbivores, and the decomposers (Swift et al. 1979), with the stability of the system dependent on the transfer of nutrients and energy among these three components. The maintenance of plant productivity is governed to a large degree by the rate at which carbon and other nutrients immobilized in dead plant and animal residues are utilized for energy and growth by the soil microflora. During the decomposition process, carbohydrates in dead plant tissue are mineralized to CO_2 via microbial respiration resulting in mass loss of the energy resource. Simultaneously, plant residues are mineralized by the activities of the microflora to nutrient elements (N, P, S, Ca, and Mg) which are eventually released into the soil solution where they become available for plant uptake.

The rate of decomposition and recycling of nutrients from dead organic matter is regulated by the composition of the microbial community and its efficiency in metabolizing the various resources available to it. In turn, microbial community structure and function is dependent on resource quality (i.e., C/N ratio, lignin content) and quantity, moisture, aeration, temperature, and pH. Alterations in resource quality, resource pH, and soil pH as a result of acid deposition would therefore be expected to effect changes in microbial community structure and function which would in turn be reflected in modifications of decay rates. The rate of decay of plant detritus, therefore, is based on the integration of all the parameters discussed in the preceding sections including qualitative/quantitative characteristics of the microbial community, C-mineralization characteristics, metabolic potential characteristics, N-mineralization activities, and enzyme activities.

Considering the potential importance of decomposition processes in maintaining plant productivity and stable organic matter reserves, it is essential that measurements of decay and nutrient mineralization rates and organic matter fluxes be included in research programs designed to elucidate the effects of acid deposition on ecosystem structure and function. There are two main approaches in determining decomposition rates. The first has been discussed previously and is based on the respiratory loss of C as CO_2 during the degradation of plant residues or soil organic matter. The second is based on the mass loss of plant residues confined in bags of specific mesh size (litterbags), which are placed in the experimental system and retrieved after various time intervals.

Ideally, mass loss measurements should be coupled with respiration measurements, because mass loss can include abiotic losses due to leaching. Quantification of nutrient elements remaining in the plant residues after various stages of decay will provide some indication of nutrient mineralization during the decomposition of a particular resource, while plant available nutrients in soil solution and nutrients immobilized in soil organic matter are readily evaluated by applying standard methods for soil chemical analyses.

Soil organic matter accumulation or depletion can be determined by measuring forest floor depth or by separating the organic horizons in a particular volume of soil, drying and weighing them, and determining ash content or soil organic C. In forest ecosystems, the ratio of forest floor mass to total annual litter input provides a measure of turnover of forest floor organic matter which can give an indication of pollutant effects on rates of organic matter decay over the long term.

Together, mass loss (litterbag) measurements made frequently over the short term, nutrient mineralization patterns, nutrient sink and availability measurements, organic matter accumulation, and organic matter residence time should give an accurate picture of any disruptions in forest floor dynamics caused by acid-forming pollutants over both the short and long term. However, in field studies where decomposition and nutrient cycling parameters are being measured to evaluate the impact of acid-forming pollutants on ecosystem functioning, it is essential to establish that prior to pollutant deposition, the polluted sites are directly comparable to unpolluted sites in terms of litter input, organic matter accumulation, and physico-chemical characteristics.

Studies which have dealt with the effects of acid-forming pollutants on the decay of plant residues, nutrient leaching, and organic matter accumulation are summarized in Table 9. With the exception of two studies (Dodd and Laurenroth 1981; Leetham et al. 1983), all investigations have focussed on forest systems or forest litter decay with the majority of them being conducted under controlled acidification conditions in the laboratory and the field.

In general, controlled laboratory studies have tended to support those conducted under controlled conditions in the field. The majority of these investigations have dealt with the impact of simulated acid rain adjusted to various acidities rather than with the relationship between litter or soil acidification and the decay process. Thus, simulated acid rain reduced decay rates of pine, spruce, and birch litter but only if extreme rainfall acidities (pH 2.0) were utilized (Ishac and Hovland 1976; Abrahamsen et al. 1977; and Hagvar and Kjondal 1981). The interaction between dosage and concentration of the simulated acid rain appears to be an important factor in controlling decay rates. Both Abrahamsen et al. (1980) and Hovland et al. (1980) reported that pH 2 or 3 rain applied at 100 mm mo^{-1} had very little effect on coniferous needle decay, whereas application of 200 mm mo^{-1} reduced decay for both rainfall acidities.

Application of pH 3.0 to 3.5 simulated acid rain to decaying coniferous and deciduous litter has produced conflicting results. Treatment of birch or mixed hardwood leaf litter with pH 3.0 rain did not alter decay rates (Hagvar and Kjondal 1981; Crist et al. 1985), whereas application of pH 2.7 or 3.1 rain to pine needles for 6 months or application of pH 3.5 rain to nine species of deciduous litter for more than 1 year stimulated decay (Roberts et al. 1980; Lee and Weber 1983). It is doubtful that decomposition was accelerated as a result of excessive leaching since both Roberts et al. (1980) and Lee and Weber (1983) reported no significant effects of acid rain treatment on cation leaching or concentrations of C, N, S, K, Ca, Mg, P, Fe, Sr, and Mn. A more plausible explanation would be that acid treatment increased erosion of the waxes and cuticles on the leaf or needle surface allowing more rapid colonization by the decomposer microflora. Also, gradual loadings of H^+ have been demonstrated to increase levels of labile C, presumably due to partial hydrolysis of the leaf litter (Killham and Firestone

Table 9 Acid deposition effects on decomposition of plant residues.

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated acid rain. Groundwater adjusted to pH 5.7, 4 and 3 with H_2SO_4 and applied at 25 and 50 mm mo^{-1} during frost-free period for 2 y Lime treatment included. Norway	Semi-podzolic soil in a sandy,glaciofluvial sediment 10-y old pine Ao-28% OM;[1] CEC=39 mEq 100 g^{-1} A_2-7.3%OM; CEC=17 mEq 100 g^{-1} B -4.3%OM; CEC=11 mEq 100 g^{-1} Field and lysimeter studies	Untreated 4.4-4.7	A[a]	-Weight loss of pine needles over 90 d in laboratory not altered by acidic rain, liming reduced decay -When needles adjusted to pH 3.5-4 with acidic H_2O, no effect on decay, adjustment to 1.8 reduced decay, at pH 1 no decay -pH 3 rain at 50 mm reduced base saturation in humus and mineral soil (0-3 cm); enhanced leaching of Ca and Mg with pH 3 and 4 rain	1
As for Ref 1	Same as for Ref 1 Pine needle decay	Adjusted needle pH: 1.0, 1.8, 3.5 4.0	A	-Decay of needles receiving pH 3 and 4 rain not affected -Adjusting needles to pH 1.8 reduced decay, at pH 1 no decay	2
Simulated acid rain Dilute solution H_2SO_4 applied at 50 and 100 kg ha^{-1} y^{-1} for 3 y at Liselbo, Sweden. At Norrliden also 150 kg H_2SO_4 ha^{-1} y^{-1}	Young pine; ground vegetation eliminated by 100 kg H_2SO_4 rain but no effect on trees. Acid rain applied to field plots. AoCEC: 22-26	pH of rain not given Untreated Ao=4.5 H_2SO_4 treated Ao=4.0, Field Ao= 3.8-4.7. With 150 kg acid: 3.6-4.3	A	-100 kg acid reduced pH of leachate in lysimeters from 5.2, 5.5 to 4.7-5.0. Enhanced leaching of S with 100 kg H_2SO_4 -Laboratory incubation of Ao soils amended with H_2SO_4 or S^o reduced CO_2↑[2] with H_2SO_4 more effective -Mineral N tended to increase with acid but nitrate was reduced -Acidification of acid forest soils slow	3
Simulated acid rain as in Ref 1	Same sites as Ref 1	Untreated: 4.1-4.7 With pH 3, 4 rain: 3.9-4.5. Below pH 3 rain: 3.7-4.1	A	-Pine needles receiving pH 3 rain decayed marginally faster than with pH 5.6 rain. Needles from trees receiving high applications of acid rain decayed faster -Spruce needles, 100 mm mo^{-1} pH 3 and 2 rain initially stimulated decay but no difference after 9 mo. With 200 mm rain, decay inhibited with pH 2 and 3 rain -pH 3.0 and 2.0 rain tended to increase loss of glucose; pH 2.0 rain increased loss of galactose, mannose -Leaching of K, Mg, Mn and P accelerated with pH 2 and 3 rain but N not affected -Decay of aspen sticks after 1 y not affected by acid rain -Humus decay reduced with increased acidification	4

continued...

Table 9 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Simulated acid rain adjusted to pH 3 or 2 with H_2SO_4 or 5.6 (distilled H_2O) Norway	Spruce needle decay in lysimeters. 100 or 200 mm mo^{-1} added twice weekly for 38 weeks	Control: 4.6-5.2 Treated: 4.2-5.1 (pH 3.0) : 2.9 (pH 2.0)	A	-With 100 mm mo^{-1}, decay stimulated initially but not after 38 wk. With 200 mm mo^{-1} acid reduced decay but differences small (4-5%) -Loss of monosaccharides not consistent; indication of reduced lignin decay with pH 2.0 rain. Acidic water increased leaching of K, Mg, Mn, and Ca. Enhanced leaching of P during latter stage of decay. Acid rain of pH lower than 3 required to reduce needle pH	5
Simulated acid rain pH 6, 4, 3, 2 rain-groundwater + H_2SO_4 in field; pH 5.3, 3 and 2 rain in lab. Ionic composition of rain adjusted. Norway	Same site as for Ref 1 Field plot received 50mm acid rain $mo.^{-1}$ May-Sept. Lab: soil cores with litter bags containing birch leaves. Cores received 10 mm 2x $week^{-1}$	Control: 4.9-5.2 pH 4 rain: 5.2-5.1 3 rain: 5.0 2 rain: 5.0-4.0 In lab: pH 2 rain reduced pH of leaves from 5.3-3.7	A	-Field: pH 2.0 rain reduced birch litter decay over 3 y In lab, pH 2.0 rain reduced litter decay but only during early stage of decay. pH 2.0 rain enhanced leaching of Ca, Mg, Mn in field and lab and K in lab. Leaching losses more pronounced in lab. N unaltered. Enhanced loss of P in well decayed litter with pH 2.0 rain. S accumulates with pH 2.0 rain. No significant effects of pH 3.0 and 4.0 rain	6
Simulated acid rain. Dilute H_2SO_4 applied as 50 and 150 kg ha^{-1} (pH 2.0 rain) annually for 6 y Sweden	Iron podzol in pine forest. Decay of pine needles, live roots over 2 y	Untreated A_{01}-A_{02}: 4.6; Treated with acid 1: 4.2 and acid 3: 4.1	A→C	-After 1 y decay of needles reduced by 1-1.5%; after 2 y 4.6-7.3% reduction in acid 1 and 2 respectively. Soluble material, lignin and total N in needles not altered by acid -Root decay reduced by acid treatments -Reduction in thickness of A_{00} by 0.5-1.0 cm in 150 kg H_2SO_4 plots; humus layer thickness reduced while A_2 increased in thickness	7[a]
Simulated acid rain 25 and and 50 kg S $ha^{-1}y^{-1}$ as dilute H_2SO_4 (pH 3.1 and 2.7 rain). Applied at rate of 5 mm bi-weekly over 6 mo period	Pine forest on podzol Mineral CEC: 2.6-9.6 OM: 0.5-5.0% Lysimeter study	3-3.8 ($CaCl_2$)	A	-H^+ and SO_4^{-}S in acid leached through litter in 2 wk, F+H in 6 wk. Not leached readily through 0-50 cm mineral soil. No cation removal over 6 mo study -6 mo decay of fresh pine needles increased by 15% in both acid treatments -Ammonium N release from L and F/H tended to increase with acidification	8
Simulated sulphuric acid rain at pH 3.0, 3.5, 4. Control rain-pH 5.6. Ionic composition adjusted. Rain applied 2.5 mm h^{-1}, 3 h d^{-1}, 3 d/week over 408 d.	Microcosms containing clay loam with pH 5.4, CEC of 32 mEq $100g^{-1}$ Thin layer of OM on surface. Decay (wt loss) of Garry oak, pin oak, big leaf maple, Oregon ash, tulip tree, sweetgum, cottonwood, willow, white elm, plane-tree	NR[4]	A→C	-With exception of plane tree litter, decomposition stimulated with pH 3.5 rain. Acid-treated pin oak leaves decayed 25x faster than untreated leaves -Of C, N, S, K, Ca, Mg, P, Fe, Sr, and Mn, only Mn was significantly affected by acid rain. After 408 days, Mn concentrations lower with pH 3.0 than 5.6 rain. Generally, decomposition (k) constants, not concentrations, affected by pH	9

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Table 9 (Continued).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
Acid rain, fog Camels Hump Mtn., Vermont	Litter accumulation (forest floor depth) along elevational gradient	NR	C	-Litter depth increased 3.5-7.3 cm, 3.8-7.1 cm and 4.5-7.8 cm in hardwood, transition and boreal zones, respectively. % organic matter increased accordingly	10
Simulated acid rain. H_2SO_4 added to adjust pH to 5.0, 4.4, 3.8, 3.4, and 3.0. Rain added once weekly at 40 ml $week^{-1}$ for 18 weeks	Mixed hardwood leaf decay, 3 mm leaf particles. Lead added in 11 concentrations and acid rain in 5	NR	A	-0-1000µg lead had no effect on leaf weight loss -pH 3-5.0 rain had no effect on litter decay	11
Acid mine drainage pH 3.7-6.3	Field study: leaf litter decay in a reservoir	NA	C	-After 21 weeks order of decay was dogwood<birch<oak<rush -Decomposition for all plant types significantly reduced in pH 3.5-4.0 stream water, and pH 5.4-6.3 water with exception of oak	12
SO_2 fumigation in the field concentrations <26, 65, 120, and 200µg m^{-3} at canopy height in control, low, med., high plots. Applied April-Oct for 5 years (<69, 174, 320, 534 ppb SO_2). Mixed grass prairie, Montana	Decay of grass litter exposed to SO_2 for 3 years. S content of leaves 590-980 µg g^{-1} for control and high plots	0-1 cm Control: 5.6 Low: 5.2 Med: 5.3 High: 4.6	A+C	-After 154 d, decay in control was 10% faster than in high SO_2 plot (76 vs 66%). High and low S content leaves in control decayed at same rate. Decay reduced due to lower soil pH and possibly toxic SO_2 derivatives on leaf surfaces	13
SO_2 fumigation 220 µg m^{-3} (587 ppb)	Decay of finely ground grass litter in laboratory	NA	A	-CO_2↑ not altered, but decay over 32 days in fumigated environment tended to reduce decay rate. Data support field study	14
SO_2 and S^0 dust emitted from gas plant; .19, .16 and .08 mg SO_2 100 cm^{-2} d^{-1} and .08 mg SO_2 100 cm^{-2} d^{-1} Whitecourt, Alberta	Three sites: 2.8, 6.0 and 9.6 km from plant. Pine forest on sandy dunes	F/H Site 1: 3.5 Site 2: 4.7 Site 3: 4.8	C	-Field CO_2↑ not different amongst sites on per square metre basis; however on organic mass basis CO_2↑ lower from site 1. Laboratory O_2↓ measurements lower from site 1 organic layers than from less polluted sites. Decay of endemic needles slowest at polluted site 1. O_2↓ of endemic needles from polluted site lower than from needles of other sites. When polluted needles were decayed in unpolluted site and vice versa, site of placement had no effect over the short term (5 mo) and slight effects over the long term (17 mo). Litterfall on per square cm basal area basis not significantly different among sites. Forest floor organic mass decreased significantly with distance from plant. Depth of forest floor greater near plant. Turnover of organic matter 5 years slower at polluted site than unpolluted site (9 vs 14 years)	15

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Table 9 (Concluded).

Pollutant and Source	Experimental Details	Soil pH	Impact	Response	Ref
SO_2 and soot from coking works, England 50 y of SO_2 exposure. 150 $\mu g\ m^{-3}$ (400 ppb) SO_2 to 200 $\mu g\ m^{-3}$ (534 ppb) SO_2 emitted currently	Brown earth, some podzolization. Sycamore woodland. Exchange experiment-polluted soil in unpolluted site and vice versa	Unpolluted soil pH 4.9 to 3.9 after placed in polluted site for 2.5 y	C	-Unpolluted soil in polluted site accumulated organic C over 2.5 y. Believed to be due to reduction in turnover of organic matter caused by inhibitory effects of pollution. Organic matter content in polluted soil placed at unpolluted site did not change over 2.5 y indicating pollutant effects are long lasting (pH increased 0.3 units over 2.5 y)	16
As for Ref 16	Sycamore litter decay measured as areal loss rather than wt loss. Litterbags with 5 and 500μm and 1 cm mesh	Unpolluted: 4.9 Polluted: 3.3	C	-Polluted and unpolluted litter decayed faster at unpolluted site than at polluted site over 12 mo. Leaves contaminated with soot placed in polluted site were slowest to decay. Contamination of litter with soot and SO_2 resulted in 35% reduction in decay - 57% of this reduction due to non-particulate pollution and 43% due to soot. Reduction in decay attributed to toxicity of soot to soil invertebrates.	17

[1] OM = organic matter
[2] ↑ = efflux
↓ = uptake
[3] A = acidic
C = chronic
[4] NR = no reaction
NA = not analysed
[5] See Ref 2 in Table 4

References:

1. Abrahamsen et al. (1977)
2. Ishac and Hovland (1976)
3. Tamm et al. (1977)
4. Abrahamsen et al. (1980)
5. Hovland et al. (1980) (similar results to Ref 4 above)
6. Hagvar and Kjondal (1981)
7. Baath et al. (1980)
8. Roberts et al. (1980)
9. Lee and Weber (1983)
10. Moloney et al. (1983)
11. Crist et al. (1985)
12. Carpenter et al. (1983)
13. Dodd and Lauenroth (1981)
14. Leetham et al. (1983)
15. Prescott and Parkinson (1985)
16. Killham and Wainwright (1984)
17. Killham and Wainwright (1981)

1982). Since rainfall acidities of pH 3.0 to 3.5 do not seem to inhibit microflora respiration (see discussion in Section 4.1), release of labile C would cause a stimulation in microbial respiration (Killham and Firestone 1982) leading to an increase in mass loss of decaying litter. Respiration measurements (O_2 uptake or CO_2 efflux) on the variously acid-treated leaf litters would have determined if stimulated decay was indeed due to an increase in microbial activity.

Long-term acidification of a pine forest floor with 50 and 150 kg H_2SO_4 ha^{-1} applied annually over a period of 6 years caused very little reduction in soil pH (4.6 reduced to 4.1), but inhibited decay of unpolluted pine needles and roots measured for 2 years after halting the acid treatments (Baath et al. 1979). Reduction in bacterial and fungal biomass, alterations in the physiological abilities of the bacterial community and shifts in the soil faunal community as a result of soil acidification probably contributed to the reduced litter decay rates. However, effects of acidification on microbial and faunal community characteristics were measured in the acidified soil and not the decaying litter so it is difficult to establish conclusively if changes in soil properties were related to reductions in litter decay. Baath et al. (1979, 1984) also reported a decrease both in humus thickness and CO_2 efflux in the humus layer of acidified plots. This is interesting since a reduction in CO_2 efflux and decay rates would be expected to result in an increase in humus layer thickness.

Field studies regarding the impact of uncontrolled acid-forming emissions on decomposition and mineralization processes are sparse. In an exchange experiment, where soil polluted by SO_2 and S-containing soot emitted from a coking plant was placed at an unpolluted site and vice versa, Killham and Wainwright (1984) found that after 2.5 years the pH of the unpolluted soil at the polluted site had decreased from 4.9 to 3.9. This was accompanied by a greater accumulation of organic C which was believed to be due to a reduction in organic matter turnover caused by the inhibitory effects of pollution. No change was recorded in organic matter content in polluted soil placed at the unpolluted site, suggesting that pollution effects on organic matter dynamics are of a relatively persistent nature. Residual effects of acidification in terms of inhibited glucose-C turnover were also reported by Lohm et al. (1984) three years after acid treatment of a pine forest was halted.

In another exchange experiment, Killham and Wainwright (1981) measured a reduction in decay (based on areal loss) of unpolluted sycamore litter placed in litter bags at a site polluted by SO_2 and S-containing soot. The decrease in decomposition rates was attributed to contamination of litter by both particulate and non-particulate pollutants which in turn had toxic effects on the soil invertebrates involved in litter decay. However, the low numbers of invertebrates (i.e., in this case the Acari and Collembola) recorded in both polluted and unpolluted sites raise some question as to their significance in influencing decomposition rates.

Perhaps the most comprehensive study on the effects of sulphur pollution on litter decomposition and organic matter turnover was performed by Prescott and Parkinson (1985). At three comparable pine sites located downwind from a gas processing plant they measured the impact of SO_2 and S^o dust on pine needle decay (mass loss), litter fall, litter accumulation, forest floor turnover, needle respiration, and forest floor respiration. In the site most affected by acid deposition, the pH of the fermentation/

humus (F/H) layer was 3.5 compared with 4.7 at the two less polluted sites. Since litterfall rates did not vary significantly amongst the sites, the increase in depth (45 mm versus 27 mm) and residence time of forest floor organic matter (14.3 years compared with 9.3 years) in the most acidified site was believed to be due to a reduction in forest floor respiration and a decrease in pine needle decay rates caused by sulphur pollution. Laboratory measurements of reduced respiration, microbial biomass, bacterial numbers, and glucose and vanillin degradation in the F/H soil from the most acidified site (Bewley and Parkinson 1984; Bewley 1986) lent support to the field observations.

The results of a litter exchange experiment in which needles from the polluted site were placed at the unpolluted site and vice versa suggested that during the early stages of decay, the chemical quality of the needles was an important factor controlling decay rates whereas environmental factors including microclimate characteristics and pollutant inputs assumed greater importance during the later stages of decay (Prescott and Parkinson 1985). Because substrate quality is a major factor controlling decay rates, alterations in the chemical nature of plant litter caused by changes in soil chemistry or plant uptake of gaseous pollutants would indirectly influence decay rates. However, the decomposition of grass litter, which had been fumigated with up to 534 ppb SO_2 so that litter sulphur contents ranged 590 to 980 $\mu g\ g^{-1}$, was not significantly affected by high S levels in the leaves (Dodd and Laurenroth 1981). Instead, reductions in soil pH from 5.6 to 4.6 and accumulation of toxic anionic solubility products of SO_2 on the leaf surfaces were believed to play a more important role in retarding decomposition.

Considering that rates of nutrient mineralization from decaying litter and organic matter determine to a large extent primary productivity, it is surprising that the impact of acid deposition on mineralization patterns of essential nutrients has not received more attention. As mentioned previously, Lee and Weber (1983) observed that in nine species of deciduous litter subjected to pH 3.5 rain for 408 days, concentrations of C, N, S, K, Ca, Mg, P, Fe, Sr, and Mn were not affected. Enchanced leaching of K, Mg, Mn, and Ca has been observed in decaying pine and birch litter, but only if the litter was treated with extremely acid (pH 2.0) rain (Abrahamsen et al. 1980; Hovland et al. 1980; and Hagvar and Kjondal 1981). High rainfall acidity (pH 2.0) has also been reported to accelerate leaching of P during the latter stages of leaf decay (Abrahamsen et al. 1980; Hovland et al. 1980; and Hagvar and Kjondal 1981).

The effects of acid deposition on N release from decaying litter are inconclusive. Roberts et al. (1980) and Tamm et al. (1977) observed that release of ammonium N tended to increase with a reduction in forest floor pH from 4.5 to 3.6. However, treatment of pine, spruce, and birch litter with pH 2 rain or acidification of a pine forest from pH 4.6 to 4.1 had no measurable effects on N release from decomposing litter (Abrahamsen et al. 1980; Baath et al. 1980; Hovland et al. 1980; and Hagvar and Kjondal 1981). The short-term nature of many of these studies and the high dosages of acid inputs involved suggest that these observations may be misleading when predicting long-term, chronic effects of acid deposition on N-mineralization. It would be expected that a reduction in litter and organic matter decay would eventually lead to a decrease in N mineralization and N availability although the relationship between organic matter decay and N dynamics is not well understood. A simulation model developed by Aber et al. (1982) to determine the potential effects of acid precipitation on soil nitrogen

and productivity of forest ecosystems tentatively predicts that under the N-limiting conditions characteristic of northern temperate forests, alterations in available N due to acid deposition could have short-term effects on primary productivity which, over the long term, are complicated by temporal changes in the production/decomposition balance governing N-mineralization. Considering the importance of N in maintaining productivity and the lack of conclusive evidence on the effects of acid-forming pollutants on N release it is essential that more research be directed to understanding the interactions between acidification, organic matter decay, N-mineralization and primary productivity. The presence of N in acid emissions would add an extra degree of complexity to these interactions.

Controlled laboratory and field studies have demonstrated that litter decomposition is retarded only if the plant residues are treated with extremely acid (pH 2.0) rain or fumigated with high concentrations (530 ppb) of SO_2. Treatment with pH 3.0 to 3.5 rain has resulted in either no effects or an enhancement of litter decay. Due to the buffering capacity of decaying litter and organic matter, high rainfall acidities (generally less than pH 3.0) are required to change litter pH. The litter acidities at which reductions in decay have been recorded are variable and include pH 1.8 and 3.7 to 4.1 for pine needles, pH 2.9 for spruce needles, and pH 3.7 to 5.0 for birch leaves. In the field, with uncontrolled inputs of acid-forming pollutants, reductions in forest floor pH from 4.8 to 3.3, 3.5, or 3.9 have resulted in decreased litter and organic matter decay accompanied by an increase in forest floor organic mass and a retardation in organic matter turnover.

Reductions in organic matter decay due to acidification would imply that nutrient mineralization would also be inhibited. However, this is not necessarily the case as evidenced by increased leaching of cations and P and no alterations of N content in acid-treated litter. The reductions in organic matter decay as a result of acid deposition and how this relates to nutrient mineralization patterns requires clarification. Also the significance of suppressed litter decay to alterations in primary productivity is unknown and warrants further investigation.

In an attempt to understand the impact of acid-forming pollutants on ecosystem structure and function, it is essential that those processes which maintain soil fertility and primary productivity - i.e., organic matter decomposition and nutrient mineralization - be investigated. However, it should be kept in mind that changes in organic matter turnover due to pollutant deposition will only be evident over the long term. Effects of acid deposition on litter decay (i.e., mass loss) are measurable over the shorter term but necessitate frequent litterbag studies so current impacts can be assessed. In ecosystems characterized by slow decomposition rates and low organic matter turnover, where the length of time required for measurable effects of pollution to become evident is very long, assessments of organic matter decomposition may not be useful for biomonitoring purposes. Where rapid assessments of pollutant stress on decomposition processes are required, glucose metabolism patterns may be a better alternative.

5. ACIDIFICATION EFFECTS ON SYMBIOTIC AND DISEASE-CAUSING MICROORGANISMS

5.1 MYCORRHIZAE

5.1.1 Introduction

Mycorrhizae are beneficial associations formed between certain fungi and the roots of green plants. Only a small portion of green plant species do not naturally form mycorrhizae and those that do include most of the major agricultural crops of the world and all of the commercially important forest trees. The mycorrhizae of forest trees have been studied for the longest period of time, 100 years, as the mycorrhizae of most conifers and many hardwoods are conspicuous to the unaided eye. Infection by the symbiotic fungi, mostly basidiomycetes and ascomycetes which include organisms which produce fruit-bodies such as toadstools and truffles, result in major morphological modifications of the fine feeder roots. In contrast, the mycorrhizae of agricultural plants and most shrubs, grasses, and forbs, are formed by phycomycetes which produce only soil-borne spores and cannot be distinguished without staining and observations with a microscope. The former type of mycorrhizae, such as those formed with pines, are called ectomycorrhizae and the latter types, such as those formed with grasses, are called vesicular-arbuscular (VA) mycorrhizae.

The major benefit of mycorrhizae to the host plant is more efficient nutrient uptake, especially with regard to low mobility ions such as phosphorus. Other benefits have been suggested such as enhanced water uptake, protection from root pathogens, increased temperature tolerance, and increased tolerance to extremes in pH; however, these conceptually attractive functions have not been unequivocally demonstrated under uncontrolled field conditions. It is without question, however, that mycorrhizal plants survive and grow much better in the field than nonmycorrhizal plants and that almost anything that interferes with the mycorrhization process is detrimental to plant performance.

The key factor in the beneficial effect on plant growth appears to be the development of fungal mycelia external to the infected root which function in nutrient uptake, i.e., an effective increase in root density or nutrient "capturing" capacity. Both single hypha and rhizomorphic aggregations of hyphae may function to adsorb and transport low mobility ions to plant roots although the latter may be more effective over long distances. Rhizomorph-forming fungi are only associated with naturally low root density plant species such as pine and spruce. It is thus of major concern to maintain the appropriate fungi in the vicinity of plant roots for nutrient uptake to function most efficiently. The degree of benefit of mycorrhizae will be dependent upon host factors, the species or strain(s) of fungus, and soil conditions. Some host species are highly dependent upon the fungus (e.g., sweetgum) and will not grow in its absence, whereas other plants (e.g., many grasses) can grow well in rich soils when nonmycorrhizal. Ectomycorrhizal hosts may be associated with only a few fungi (e.g., alders) whereas other species may be associated with many hundreds of fungi. In the case of VA hosts, there appears to be little taxonomic specificity on an infection basis but perhaps specificity on a functional level.

Under identical conditions different endophytes will produce quite different responses in the hosts, with some benefiting performance to a much greater degree than others. These may be due to inherent efficiency factors of the endophyte (infection rates, external mycelium development, uptake and transport of nutrients; Abbott and Robson 1984) or interactions with soil conditions. It is clear that certain VA mycorrhizal fungi and probably ectomycorrhizal fungi are more effective in some soils than others; however, the causes of these differences remain obscure. Of the possible causes, soil phosphorus levels and to a lesser extent, soil pH, have been investigated.

5.1.2 Soil pH and Mycorrhizae Formation and Function

Although soil pH is one of the most commonly measured parameters, there is a paucity of studies on the influence of pH on mycorrhizal associations. Thus, existing data on pH per se does not exist to provide a predictive basis for effects of inputs of acid forming emissions on mycorrhizae of agricultural and forest plants. Nonetheless, several studies suggested that soil acidification might result in alterations of mycorrhizal status or function.

Wang et al. (1985) studied the long-term (22 year) effects of liming an acid (pH 4.5) soil to pH 7.5 on the VA mycorrhizae of oats. Overall infection levels between the two soils did not differ but in the acid soil the infections were all caused by the "fine endophyte" and in the limed soil all infections were caused by coarse endophytes. Similar effects were found when the acid soil was abruptly limed, i.e., the pH effects on the endophytes were sudden and persistent. In contrast, Davis et al. (1983) found that in soil adjusted to a range of pH's from 5 to 8, that both Glomus mosseae and G. fasciculatum infected the roots of sweetgum in all treatments. However, the effectiveness (i.e., growth promoting effect) of each species varied with pH. Glomus mosseae was largely ineffective at pH 5 but produced a strong growth response at pH 6 and above, whereas G. fasciculatum was most effective in acid soils. Similar results were found with a tropical legume by Huang et al. (1983). In a soil adjusted to pH 5.2, 5.7 and 7.4, inoculation with G. fasciculatum resulted in positive growth responses at all three pH levels whereas G. mosseae and G. etunicatum only produced a growth response at pH 7.4.

In a more detailed examination between VA mycorrhizae effectiveness and soil pH, Hayman and Tavares (1985) tested nine fungi in two soils adjusted with lime to pH 4, 5, 6, and 7. In general, mycorrhizal development was high regardless of the fungal species used or soil pH. However, plant response was highly dependent upon an interaction between each particular fungus and soil pH. At pH 4, only one species (Glomus clarum) produced a substantial growth response and it was ineffective at pH 7. Glomus mosseae was most effective at near neutral pH's and much less effective in acid soils. Those species most effective under acid conditions were least effective at pH 7 although G. fasciculatum was highly effective in both soils from pH 5 to pH 7. Nonetheless, this study illustrates that root colonization may be little affected by small changes in soil pH, but effectiveness in promoting plant growth is a much more pH (acidity) sensitive character. Hayman and Tavares (1985) suggested that the difference between extensive infection and effectiveness is the ability of fungi to proliferate in the buffered rhizosphere but the inability to develop the extramatrical hyphae necessary for phosphate uptake from the surrounding soil matrix.

The effect of soil acidity on the development and functioning of ectomycorrhizae remains in a speculative stage. A large number of in vitro studies have been done on a range of ectomycorrhizal fungi but comparable studies of ectomycorrhizae in nonsterile soils are lacking. Hung and Trappe (1983) have summarized the in vitro studies of 31 species which show that minima for growth is generally between pH 2 and pH 3 and the optima between pH 3.5 and pH 5. In Hung and Trappe's (1983) growth experiments on nine species, seven grew well at pH 3. These in vitro experiments show a tolerance of ectomycorrhizal fungi to strongly acid conditions but the response of ectomycorrhizae to acidity in terms of formation and effectiveness remains to be determined.

5.1.3 Mycorrhizae and Acid Forming Emissions

In that mycorrhizae are instrumental in the acquisition of mineral nutrients by most forest, range, and agricultural plants, attention has recently been focussed on the question of whether acid forming emissions could adversely affect this key symbiotic association. Some observations in areas experiencing forest decline suggest that this may be the case. Klein (1984) states that they have failed to observe ectomycorrhizae on red spruce at the higher elevations of Camels Hump where forest decline symptoms are obvious. This statement was not substantiated with any data but if true could imply that the loss of mycorrhizae could be partially responsible for forest decline. Ectomycorrhizae, fine roots, and potential root pathogens of spruce have been studied in more detail in forest decline areas of Europe. Liss et al. (1984) found a positive correlation between crown damage and decline of fine roots and ectomycorrhizae. They concluded that the decrease in root mass was due to reduced carbon allocation to the roots, i.e., a result rather than cause of foliage dieback. Livingston and Blaschke (1984) also found the least number of active ectomycorrhizae on the most affected spruces.

A second approach used to study possible effects of acid forming emissions on mycorrhizae has been to expose mycorrhizal plants to SO_2 or to apply artificial acid rain and to monitor effects on plant growth and mycorrhizae (Table 10). The only study on SO_2 fumigation was performed by Mahoney et al. (1985) utilizing ectomycorrhizal and nonmycorrhizal loblolly pine seedlings. The short term fumigation had no effect on the ectomycorrhizal seedlings. However, fumigation resulted in reduced root growth of nonmycorrhizal plants. The authors point out that, as nearly all plants in nature are mycorrhizal, experimental results on nonmycorrhizal plants should not be extrapolated to the field.

Shafer et al. (1985) applied simulated acid rain varying in pH from 2.4 to 5.6 to loblolly pine seedlings in the greenhouse. They recorded small differences in both percentage of ectomycorrhizal short roots and shoot growth. These differences did not appear to be strictly related to the rain applications and would probably be insignificant in field situations. In a similar study, Stroo and Alexander (1985) studied the effect of acidified rain on ectomycorrhizal development of white pine either inoculated with Pisolithus tinctorius or planted in nine forest soils in the greenhouse. In three of the nine soils, applications of rain at pH 3.5 resulted in slightly enhanced ectomycorrhizal formation and increased shoot growth occurred in one soil after application of acidified rain. When above ambient amounts of acidified rain were applied to the

Table 10. Effects of SO_2 or simulated acid rain on mycorrhizal and nonmycorrhizal plants.

Treatment	System	Final or Δ Soil pH	Effects	Ref
SO_2 60 ppb 6h day^{-1}, 5 weeks	Pine seedlings ± *Pisolithus*, greenhouse	NR[1]	-Mycorrhizae:0 -Shoot growth:- -Root growth:0	1
Rain, 37X over 16 weeks, pH 5.6,4.0,3.2, & 2.4	Pine seedlings, greenhouse	6.5,6.7 6.4,5.0	-Mycorrhizae:2.4> 5.6 > 3.2 > 4.0 -Shoot growth 2.4 > 5.6 > 4.0 > 3.2	2
Rain, 2X/week 13 weeks, pH 5.5 4.0,3.2, & 2.8	Soybean + *Glomus*, field, soil pH 6.3	5.3,5.4 5.4,5.4	-Mycorrhizae:0 -Plant growth:0 -Lesions on leaves if pH 2.8 "rain"	3
Rain, 3X/week 16 weeks, 1X ambient, pH 3.5 & 3.6	Pine, 9 forest soils, greenhouse	NR[1]	-Mycorrhizae:+ 3/9 -Plant growth:+ 1/9	4
Rain 3X/week 16 weeks, 3X ambient, pH 3.5 & 5.6	Pine ± *Pisolithus*, greenhouse	NR	-Mycorrhizae:-(< root growth also), if nonmycorrhizal < shoot & root growth	4
Rain, 2X/week 14 weeks, pH 3,4, & 5.6	Grass ± *Glomus*, greenhouse, sandy loam pH 6.4	<0.2,0.8 & 2.2 units	-Plant growth:0 -Mycorrhizae:NR	5

[1]NR = not reported

References:

1. Mahoney et al. (1985)
2. Shafer et al. (1985)
3. Brewer and Heagle (1983)
4. Stroo and Alexander (1985)
5. Killham and Firestone (1983)

seedlings, root growth and percent mycorrhizae formed by Pisolithus were decreased; as well, shoot and root growth of nonmycorrhizal plants were decreased. It should be noted that all plants were small and that the rates of infection for all plants were low, usually less than 30%.

In two experiments utilizing VA mycorrhizae no effects of simulated acid rain were detected. In a field experiment, Brewer and Heagle (1983) applied rain varying in pH from 2.8 to 4.0 to soybeans inoculated with Glomus geosporum (plus ambient rain). Although the most acidic rain resulted in lesions on the leaves, plant growth and mycorrhizal development were unhindered. Killham and Firestone (1983) used similar rain acidities on inoculated and noninoculated grasses and found no differences in plant growth due to inoculation. No measurements were made of the degree of mycorrhizal development.

The studies done on simulated acid rain or SO_2 usually have not resulted in soil acidification when ambient concentrations were used. However, soil acidification does occur in the case of sulphur dust contamination in the vicinity of gas plants in Alberta and a study has been made of the mycorrhizal infection potential of soils contaminated with different amounts of sulphur dust (S. Visser, unpublished data). Samples of FH horizons and surface 10 cm of mineral soil were collected in a lodgepole pine stand at different distances from the sulphur source and a VA mycorrhizal plant, timothy, and an ectomycorrhizal plant, lodgepole pine, were planted in each sample and grown in the greenhouse. The organic layer was strongly acidified, with the pH as low as 1.7 where contamination was heavy. Acidification of the mineral soil was less extreme with the most acidic sites being between pH 3.5 and 4.0. The minimum pH at which growth of timothy occurred was pH 3.6 and the minimum for VA infection was pH 4.1 to 4.3. All timothy plants growing in soils with a pH above 4.5 were heavily infected. The lowest pH at which the pines would grow was 2.8 and the most acid soil in which ectomycorrhizae formed was pH 3.3. Some ectomycorrhizal fungi were apparently more sensitive to acidity than others, e.g., E-strain, Mycelium radicis atrovirens and Suillus were almost exclusively found in the less acid samples. It was apparent from this study that mycorrhizae can develop under very acid conditions and that conditions must be extreme in order to affect mycorrhizal root colonization. However, the effectiveness of the mycorrhizae may have been impaired by the acid conditions as observed by Hayman and Tavares (1985).

In conclusion, there has been no evidence presented that acidified rain or SO_2 has any significant direct effect on mycorrhizal associations. In order to prevent development or cause a change in the endophytes, it would be necessary to have extreme changes in soil pH. Changes in VA mycorrhizal efficiency might occur with less dramatic changes (0.5-1 pH unit) but, nonetheless, demonstrable changes in soil chemistry would precede mycorrhizal changes.

5.2 LEGUME-RHIZOBIUM SYMBIOSIS

Plants which are capable of fixing atmospheric nitrogen (N) play important roles in both natural and agricultural ecosystems. Nitrogen is often the factor limiting soil productivity and its ultimate supply is partially dependent upon either the fixation of N_2 by free living bacteria and blue-green algae or by nodulated plants (legume-Rhizobium

or nonleguminous-Frankia associations). In agriculture, legumes are very often used to maintain or enhance soil fertility and it is considered essential to utilize legumes for both forage crops and to minimize the use of chemical fertilizers. One factor that has a strong influence on the development of the Rhizobium symbiosis is soil pH and the other soil-acidity factors, Ca deficiency, and Mn and Al toxicity (Munns 1977). Alexander (1985) has argued convincingly that N_2-fixation is limited not by the absence of effective organisms but by ecological constraints on the process and that soil acidity is a major factor limiting legume cultivation. Soil pH's below 6 adversely affect the survival of Rhizobium (Lowendorf 1980) and nodulation (Alexander 1985). Even if nodulation does occur under regimes of acidity stress, N_2-fixation may be inhibited with resultant poor growth of the host (Munns 1977). Relatively small differences in soil pH can account for large differences in nodulation and nodulation function. Munns (1977) illustrates a decrease from near maximum nodulation in Australian soils of pH 5.0 (measured in $CaCl_2$) to near minimum at pH 4.5. In Alberta soils nodulation and yield of alfalfa decreased sharply when the soil was more acid than pH 6 (Rice et al. 1977). In contrast, nodulation and growth of red clover in the same soils were insensitive to pH differences between 4.5 and 7.2. It is clear that the so-called acid intolerance of legumes is not simple and involves interactions of host tolerance, Rhizobium sensitivity (Rice 1982), and soil chemical characteristics. Nonetheless, from data on soil acidity and legume performance, it might be anticipated that inputs of acid emissions might have adverse effects on N_2-fixation and plant growth.

To date, no studies have been made on the effects of SO_2 on the legume-Rhizobium symbiosis and only a few studies completed on the effects of simulated acid rain. The results of simulated acid rain are somewhat conflicting, probably due to the very different experimental techniques (Table 11). Shriner and Johnston (1981) observed a sizeable decrease in soil pH in greenhouse studies and no change in field studies. Although nodulation was decreased in both situations by pH 3.2 rain, there were no effects on plant growth or rates of N_2-fixation. Other aspects of this study illustrate some of the difficulties of acid rain studies, e.g., rain adjusted to either pH 6 or 3.2 substantially reduced nodulation when applied to the foliage only as compared to application to the soil only. Chang and Alexander (1983a) also observed decreased nodulation with simulated acid rain in an acid soil. However, the "control" rain resulted in increased soil pH which would have enhanced nodulation. In other studies, no effect was noted on nodulation by rain above pH 3 (Porter and Sheridan 1981; Heagle et al. 1983) even when exposures were as long as two years.

Although the legume-Rhizobium symbiosis would be anticipated to be one of the systems more sensitive to acidic inputs, no experimental evidence to date indicates that adverse effects have occurred even when extremely acidic solutions have been applied. However, if soil acidity is increased by acid emissions, not only nodulation but N_2-fixation should be carefully monitored.

5.3 DISEASE DEVELOPMENT

The effects of air pollutants, including SO_2, on plant parasites and diseases have been reviewed by Heagle (1973), Treshow (1975), Shriner and Cowling (1980), Huttunen (1984), and Smith et al. (1984). Numerous studies have been reviewed which document

Table 11. Effects of simulated acid rain on nodulation and N_2-fixation of legumes.

Treatment	System	Final or Δ Soil pH	Effects	Ref
Rain, 1-17 weeks, 3X/week pH 3.2 & 6	Bean & soybean + *Rhizobium* field and greenhouse, pH 4.9	No Δ or 1 unit	<nodulation at pH 3.2, no Δ plant growth, no Δ N_2-fixation	1
Rain, tops only, 7X, pH 2,3,4,5 & 6	Alfalfa + *Rhizobium* growth chamber, Perlite	NA[1]	<N_2-fixation at pH 2, <shoot mass at pH 2, >nodulation at pH 2	2
Rain, 2 years, 2X/ week pH 5.5, 4, 3.2, 2.8, + ambient	Soybean + *Rhizobium*, field, pH 5.9	5.8,5.8,5.8 5.5	No Δ plant growth, nodulation; foliar injury below pH 3.3	3
Rain, 100 cm pH 3.5, 4.1, 5.6	Clover and trefoil + *Rhizobium*, soil pH 4.6	Variable, changes small	<nodulation and plant growth with pH 4.1 or 3.5 rain	4

[1]NA = Not applicable

References:

1. Shriner and Johnson (1981)
2. Porter and Sheridan (1981)
3. Heagle et al. (1983)
4. Chang and Alexander (1983a)

demonstrable effects of SO_2 on plant diseases; however, it is crucial to bear in mind that the levels of SO_2 responsible would not be permitted under current legislation.

Heagle (1973) cited only one study done under controlled conditions with the remainder being field studies of plants in polluted areas without adequate controls. He found that SO_2 pollution resulted in the decreased incidence of 13 of 16 diseases and an increase in the incidence of three diseases. His general conclusions were that plants were more sensitive to pollutants than the parasites and that pollution stress decreased obligate parasitism and increased facultative parasitism.

Since Heagle's review, more emphasis has been placed on controlled fumigations and on the effects of simulated acidified rain on plant pathogens and diseases (Table 12). The results have been variable and the effects have generally only been found when either SO_2 concentrations were very high or the rain very acid. Little can be predicted from these acute situations to chronic field conditions.

Effects on disease development may be due to direct effects on the pathogen or due to indirect effects by altering structural, physiological, or metabolic factors of the host (Treshow 1975). Direct effects on the pathogens have usually been evaluated using very high concentrations of SO_2. The studies cited by Treshow (1975) utilized SO_2 concentrations that ranged from 1 to 2500 ppm and thus are not applicable to field situations. Studies with acidified rain have also all utilized excessively acid solutions which often result in lesions on the foliage, conditions not recorded in the field. Nonetheless the evidence is clear that industrial SO_2 pollution can inhibit or prevent certain diseases. In Britain it has been shown that sycamore tarspot, a foliage disease, is completely absent in areas where SO_2 concentrations exceed 35 ppb (Bevan and Greenhalgh 1976). However, it has been pointed out by Treshow (1975) and Huttunen (1984) that concentrations of SO_2 that have been observed to control diseases in the past are now rare due to increased air pollution standards.

It has been suggested that root diseases might be partially responsible for the widespread forest decline in Europe and eastern North America (Livingston and Blaschke 1984). In German forests the fine roots of spruce trees exhibiting varying degrees of severity of forest decline symptoms have been examined in detail. Liss et al. (1984) found a positive correlation between foliar damage and decline in fine roots with the decline most pronounced in the deep rooting zone. However, the effects were likely due to the decrease in photosynthetic capacity of the trees and not visa versa. Livingston and Blaschke (1984) also examined fine roots of spruce for pathogenic fungi but could find no evidence that root pathogens were responsible for forest decline. Mycelium radicis atrovirens, which is considered to be a pathogen by some investigators (Richard and Fortin 1974) and an ectomycorrhizal symbiont by others (Thomas and Jackson 1979), occurred equally on trees showing mild and severe decline symptoms. Carey et al. (1984) recorded the facultative parasite Armillaria mellea on roots of declining red spruce in Vermont but concluded that mortality was independent of its presence.

Evidence to date does not allow for a clear assessment of the effects of acid-forming emissions on plant diseases, particularly under chronic conditions. The conclusions reached by Smith et al. (1984) still apply to current situations. They concluded, among other things, that: (1) foliar or stem diseases are the most likely diseases to be affected because the pathogens spend a significant time on the surface of

Table 12. Effects of SO_2 or simulated acid rain on disease development.

Treatment	System	Final or Δ Soil pH	Effects	Ref
SO_2 200 ppb, 6h	Pine + brown spot needle blight, greenhouse	NR[1]	>lesions	1
Rain, ambient, 2 weeks pH 2.5, 3.5 & 4.5	Tomato + bacterial speck greenhouse, soil mixture	NR	Acidic lesions at pH 2.5, 0 at pH 3.5 <bacterial speck <plant growth	2
Rain, 4 weeks pH 3.2 & 6	Beans + haloblight greenhouse, potting mixture	NR	> or <disease <shoot,>root mass	3
Rain, 4 weeks pH 3.2 & 6	Oak + rust greenhouse, potting mixture	NR	<disease	3
Rain, 3 weeks pH 3.5 & 7	Corn + corn blight greenhouse	NR	> or <symptoms	3
Rain, 9 weeks pH 3.2 & 6	Beans + halo blight field	NR	> or < symptoms	3
Rain, 9-12X, 4 weeks, pH 5.6, 4.0, 3.2 & 2.4	Lupine + Phytophthora greenhouse, pH 6.1	6.1,6.2,6.0, 5.2	> acidic lesions at pH 2.4, none on disease	4
Immersed in pH 5.6, 5, 4.0 & 3.0 for 2 days	Fir + Phytophthora,	5.3,5.3, 5.2, 3.9	<disease at pH 3	4

continued...

Table 12 (Concluded).

Treatment	System	Final or Δ Soil pH	Effects	Ref
SO_2, urban pollution	Sycamore tar spot	NA[2]	No disease when SO_2 >35 ppb	7
Rain, 3 x 6 min pH 3, 4 & 5.6	Beans + anthracnose	Δ=0	>disease at pH 3	5
SO_2, 48 h, 40 ppb	Rose black spot	NA	<lesions	6
SO_2, 150 ppb 8 days	Bean + rust Tomato + blight Greenhouse	NR	< rust, none on blight	8

[1]NR not recorded
[2]NA not applicable

References:

1. Weidensaul and Darling (1979)
2. Bisessar et al. (1984)
3. Shriner (1978)
4. Shafer (1983)
5. Smith et al. (1984)
6. Saunders (1966)
7. Bevan and Greenhalgh (1976)
8. Weinstein et al. (1975)

the host and are thus most exposed to pollutants; (2) forest vegetation would be more likely to be affected than agricultural vegetation due to the aggressive pesticide programs used in agriculture which would minimize any pollution-disease interactions; and (3) the threshold pH for acidic rain is about pH 3.5-4.0, above which little effect would be anticipated. In addition, there is no evidence that root pathogens are directly responsible for forest decline; rather they are affected indirectly by changes in soil chemistry or host resistance.

6. CONCLUSIONS

It is apparent from this review that almost without exception (one being stem and leaf diseases), a change in soil pH is necessary to promote a change in the micro-organisms or microbially-mediated processes. This has not always been recognized, as evidenced by the absence of soil pH measurements in many of the studies cited herein. By the measurement of this one simple parameter it should thus be possible to predict the likelihood of soil process changes and the acid emission loading required to initiate the changes. Calculations based on known emission inputs (currently being measured) and soil characteristics should be made to determine the time required to produce a range of changes in soil pH. This information, combined with the experimental evidence on critical or threshold pH values for microbiological changes will indicate which, if any, of the microbiological factors should be included in acid emissions effects studies. Based on over 100 studies conducted primarily in North America and Europe, critical pH values and other conclusions for key microbial functions are summarized below:

1. Microbial communities

The majority of studies dealing with the impact of acid deposition on qualitative and quantitative aspects of the soil microbial community have dealt with chronic effects in the field and therefore, the results may be applicable to some Alberta soils. In summary, it can be concluded that:

a. Effects of S-pollutants in forest systems are usually restricted to the organic mat unless the mat is thin, thereby making the underlying mineral soil more susceptible to acidification. Also, S^{o} dusting may accelerate the acidification of the forest floor to such an extent that the mineral soil is also rapidly acidified.

b. Pollution of forest soils with S^{o} dust for a minimum of 3 years will result in rapid acidification due to the stimulation of S-oxidizing thiobacilli. In agricultural soils in Alberta, S-oxidizing thiobacilli require 2-3 years to manifest themselves after the introduction of a S source.

c. Acidification of a naturally acidic forest soil to approximately pH 3.0 or less results in a significant reduction in total microbial biomass. Bacteria are adversely affected at pH<4.0; fungi appear to be less sensitive to acidification but this may be an artifact due to methodological problems.

d. The impact of S pollutants on fungal community structure and the role of fungi in the oxidation of S^{o} dust are largely unknown and require additional research.

Pollutant effects on microbial community structure provide little insight into the effects on microbial processes such as decomposition and nutrient cycling. However, coupled with other measurements such as glucose stimulated respiratory activity, substrate utlization rates, and decay rates of plant residues, the qualitative/quantitative aspects of the microbial community provide a more holistic picture and a better understanding of pollutant-microbial interactions.

2. Soil respiration

Based on the results from both laboratory and field investigations, it appears that a reduction of naturally acidic forest soils to pH 3.0 or less will have an inhibitory effect on soil respiration. Due to the high buffering capacity of decaying plant residues and organic matter in the forest floor and the probable adaptation of an already acid-adapted microflora to further acidification, application of high dosages of SO_2 or extremely acid rain (i.e., pH 2.0) are necessary to reduce the soil pH to such an extent that microbial respiration is altered. However, respiration measurements are not necessarily the most sensitive indicator of pollutant stress on the microbial community. Shifts in microbial community structure may take place with no obvious effects on soil respiration as a pollutant-insensitive component of the microflora replaces a sensitive one. However, on the basis of soil respiration determinations, the decay function of the soil microflora in forest soils is affected only when acidification stress is severe. Whether this is true in agricultural systems, where a more acid-sensitive microflora may predominate, remains to be determined.

3. C-mineralization

It appears that glucose mineralization patterns may be the best approach to identifying the effects of acid-forming pollutants on the metabolic potential of the decomposer microflora. Vanillin decay patterns may be more sensitive but additional research is required before this can be stated unequivocally. The relevance of pure substrate decay measurements to general decomposition and mineralization of plant residues in the field is uncertain. In Alberta, a reduction in glucose, cellulose, and vanillin decay as a result of acidification has been measured in the laboratory and this may be an indication of reduced organic matter decay in acidified soil in the field. However, this can only be substantiated by comparing decay rates of pure substrates and plant residues in the laboratory and the field. It is necessary to reduce the soil pH to approximately 3 before changes in C-mineralization can be detected.

4. Decomposition

Controlled laboratory and field studies have demonstrated that litter decomposition is retarded only if the plant residues are treated with extremely acid (pH 2.0) rain or fumigated with high concentrations (530 ppb) of SO_2. Treatment with pH 3.0 to 3.5 rain has resulted in either no effects or an enhancement of litter decay. Due to the buffering capacity of decaying litter and organic matter, high rainfall acidities (generally less than pH 3.0) are required to change litter pH. The litter acidities at which reductions in decay have been recorded are variable and include pH 1.8 and 3.7 to 4.1 for pine needles, pH 2.9 for spruce needles and pH 3.7 to 5.0 for birch leaves. In the field, with uncontrolled inputs of acid-forming pollutants, reductions in forest floor pH from 4.8

to 3.3, 3.5, or 3.9 have resulted in decreased litter and organic matter decay accompanied by an increase in forest floor organic mass and a retardation in organic matter turnover.

Reductions in organic matter decay due to acidification would imply that nutrient mineralization would also be inhibited. However, this is not necessarily the case as evidenced by increased leaching of cations and P and no alterations of N content in acid-treated litter. The reductions in organic matter decay as a result of acid deposition and how this relates to nutrient mineralization patterns requires clarification. The significance of suppressed litter decay to primary productivity is unknown and warrants further investigation.

In an attempt to understand the impact of acid-forming pollutants on ecosystem structure and function, it is essential that those processes which maintain soil fertility and primary productivity - i.e., organic matter decomposition and nutrient mineralization - be investigated. However, it should be kept in mind that changes in organic matter turnover due to pollutant deposition will only be evident over the long term. Effects of acid deposition on litter decay (i.e., mass loss) are measurable over the shorter term but necessitate frequent litterbag studies so that current impacts can be assessed. In ecosystems characterized by slow decomposition rates and low organic matter turnover where the length of time required for measurable effects of pollution to become evident is very long, assessments of organic matter decomposition may not be useful for biomonitoring purposes. Where rapid assessments of pollutant stress on decomposition processes are required, glucose metabolism patterns may be a better alternative.

5. Soil enzymes

The studies performed to date suggest that the activity of most soil enzymes is adversely affected by acidic deposition only if high dosages of extremely acid (pH 2.0) rain are applied to the soil. This is in agreement with soil respiration measurements which also appear to be sensitive to rainfall acidities below pH 3.0. Considering the ease with which soil respiration can be measured compared with the difficulties involved in the assaying and interpretation of soil enzyme activity, in an acid deposition biomonitoring program emphasis should be on measurements of soil respiration rather than on soil enzymes.

6. Ammonification

There is little reduction in the rates of ammonification until the soil pH reaches 3 or less. Chronic inputs of acid-forming emissions would not be anticipated to produce measureable changes in the rates of NH_4^+ production but might alter the conservation of N and levels of NH_4^+ in soil if nitrification is inhibited.

7. Nitrification

The nitrification process is definitely inhibited by increasing acidity below pH 5 to 6. In forest soils that are already acidic this may be of little consequence because the primary mineral form of N is NH_4^+ and is readily available to plants. Even in acidic soils down to pH 4, nitrification occurs to a small extent, perhaps heterotrophically. However, in agricultural soils it is unlikely that the pH would be allowed to drop to inhibitory levels, because acidic inputs are easily compensated for by liming.

8. N_2-fixation

Little has been done with regard to N_2-fixation by free-living organisms and acid emissions. However, it would be a sensitive process as it is performed by prokaryotes and N_2-fixation is generally inhibited below pH 6. Nonetheless, inputs of N via freeliving N_2-fixers is small and the chance of detecting emission-induced changes are remote. In contrast, inputs from symbiotic N_2-fixation may be large and directly related to plant productivity. It is clear that the legume-*Rhizobia* symbiosis for some crop plants in Alberta is pH sensitive. As N_2-fixation may decrease abruptly below pH 6, this should be a prime microbiological factor to evaluate in acid emission studies.

9. Plant pathogens

The effect of acid emissions on plant pathogenic relationships would appear to be very small under chronic regimes. Efforts would be best spent in evaluating leaf and stem diseases in unmanaged ecosystems.

10. VA mycorrhizae

It would appear worthwhile to conduct studies on VA mycorrhizal plants if it is anticipated that there will be significant changes in soil pH or host resistance. These should include qualitative evaluations (species changes) and changes in function (plant growth response). Assessments of degree of infection would appear to be of little value where soil acidity is concerned. In Alberta, which is species-poor with regard to VA mycorrhizal fungi (Zak et al. 1982; Visser et al. 1984, 1985), small shifts in pH (0.5 - 1.0 unit) might result in ill-adapted and poorly functional mycorrhizae. This would be less likely where more taxonomic diversity of the VA mycorrhizal fungi exist.

11. Ectomycorrhizae

Most ectomycorrhizal plants are associated with a very diverse array of fungal symbionts which probably provide an effective buffer against environmental changes. In addition, due to the currently impossible task of identifying all but a few ectomycorrhizae (host + fungus), changes,

should they occur, could not be detected unless extreme. It would therefore be unreasonable to pursue field studies on ectomycorrhizae where acid forming emissions are chronic. It would be useful, however, to determine the effects of soil acidity on either well defined laboratory systems and/or on field areas in which extreme changes in soil pH have occurred.

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